CHEMISTRY LIBRARY
Dec 13 1957
DEC 12 1957
LIBRARY

JOURNAL

OF THE

INDIAN CHEMCIAL SOCIETY

VOL. XXXIV SEPTEMBER, 1957 No. 9

CONTETNS

		PAGE
118.	Studies on the alkaloids of *Alangium lamarckii*, Thw.—By N. K. Basu and K. D. Gode	629
119.	Studies in the behaviour of bi-univalent salts in aqueous solutions. Part XI. Barium acetate. By B. Nayak and B. Prasad	640
120.	The kinetics of the ferric thiosulphate reaction. Part I.—By D. Patnaik, C. Nanda and K Bakshi	643
121.	Light scattering in soap-solvent systems. Part II. Sodium stearate in octyl and in decyl alcohol : Intensity measurements.—By K. P. Buch	650
122.	Preparation of 2-arylamino-4-(2-thienyl)-thiazoles and their azo and mercurated derivatives.—By G. N. Mahapatra and M. K. Rout	653
123.	Studies in indigoid dyes. Part XXI. 1 : 8-Naphthapenthiophene-phenanthrene-indigos.—By Paresh Chandra Dutta and Sunil Kumar Roy	660
124.	Kinetics of the reaction between formaldehyde and ammonia.—By Sameer Bose ...	663
125.	The influence of amino-acids on the autoxidation of ascorbic acid.—By P. C. Rakshit, B. C. Sen and P. K. Bhattacharyya	668
126.	Citrate complex of cadmium.—By Rabindra K. Pattanayak and S. Pani ...	673
127.	Hydration of aluminium oxide sols.—By A. K. M. Trivedi, K. M. Buch and M. J. Patani	683
128.	Possible antiamoebic agents. Part III. Mannich bases from thiochroman-4-ones.—By A. B. Sen and Yashwant D. Kulkarni	687
129.	An analysis of the neutralisation curves of the colloidal acids. Part III.—By S. L. Gupta	691
130.	An analysis of the neutralisation curves of the colloidal acids. Part IV.—By S. L. Gupta	696
131.	Viscosity of poly-2-vinylpyridine in acetic acid.—By Bimal Bandhu Mukherjee and Mihir Nath Das	702

Short notes :

	The solubility of lead monoxide in perchloric acid and the formation of basic lead perchlorate in solution.—By R. K. Pattanayak and S. Pani ...	709
	Parachor of orthophosphoric acid.—By V. G. Vaidya and B. K. Maheshwari ...	711
	On the composition of silver citrate.—By Krishna C. Mathur and Arun K. Dey ...	713

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY
92, UPPER CIRCULAR ROAD, CALCUTTA 9.

READY DELIVERY

"SICGOL"

LABORATORY GLASSWARE

Made of

BOROSILICATE GLASS HAVING HIGH SILICA NAD LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

SARTORIUS

"SELECTA" BALANCES

Micro and Projection Types

CARL-ZEISS

REFRACTOMETESR

PSECTROPHOTOMETER

STEREO-MICROSCOPES

MUIRHEAD

POTENTIOMETER

"K-9"

TRIANGULAR BEAM

CIRCULAR ARRESTMENT

ANALYTCIAL BALANCE

CAPACITY : 200 Gms.

SENSITIVITY : $\frac{1}{10}$ Mgm.

5 Divisions throw of pointer for addition of 1 Mgm.

CARL-ZEISS

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

LEYBOLD'S

VACUUM PUMPS

HERAEUS- OVENS

JULIUS PETER- BOMB CALORIMETER

HOPPLER- VISCOMETERS

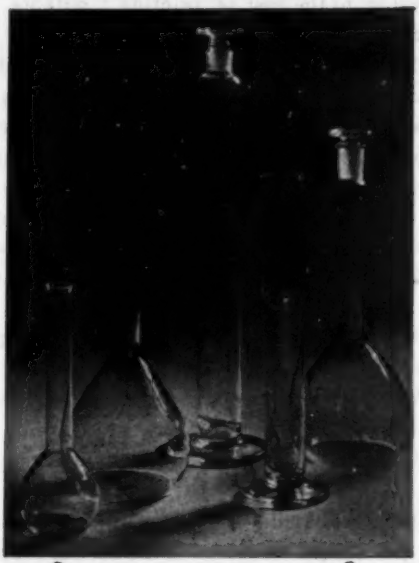
Distributors :

ADAIR, DUTT & Co. (INDIA) PRIVATE Ltd.

CALCUTTA MADRAS BOMBAY NEW DELHI

SCHOTT & GEN MAINZ JENAer GLAS

LABORATORY WARES MADE OF JENAER GERAETEGLAS 20



Since its introduction in 1920 it has become universal glass for the chemist, as it combines in the most favourable way all chemical, thermal and mechanical properties demanded of a high quality laboratory glass. On account of its low coefficient of expansion, the Geraeteglas 20 successfully withstands temperature changes. It has the highest stability to water and acid of all laboratory glasses known up to now and belonging to the 1st hydrolytic class, is extremely resistant to attack by alkalies and shows mechanical hardness against scratching. Such combination of the most important features makes this glass indispensable for any chemical analysis of high precision, microchemical and microanalytical work, and research in the alkaline field as well as work with sensitive biological substances.

Sole Distributors:

THE SCIENTIFIC INSTRUMENT Co. Ltd.

ALLAHABAD, BOMBAY, CALCUTTA, MADRAS, NEW DELHI.

Information for Authors

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Upper Circular Road, Calcutta-9.

2. A paper will not normally be considered for publication in the Journal unless at least one of the authors or authors is (are) either a Fellow or an Associate member of the Society.

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. All papers should be submitted *in duplicate* in typescript with double line and marginal spacings. Tables and foot notes add considerably to the cost of printing ; authors are requested therefore not to use them unless necessary.

5. All papers should be carefully revised and should be absolutely in final form of printing. Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field Extensive review of literature should be avoided. Well known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm., c.c., ml., g., m.p , b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenever possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its "List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline); year of publication; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, 17, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.*, 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form: "Found:———; ———. ——— requires ——— per cent". Analytical results for compounds which have been previously known should be given in the form: "Found:——; ———. Calc. for———: ———; ———."

12. Every paper should be accompanied by a short abstract giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the investigation and normally should not exceed 250 words.

13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, which should be returned whithin a week to the Hony. Secretary, failing which it will be directly printed.

14. Authors will get 50 copies of reprints free of charge and extra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs. It would be desirable to inform him when the manuscript is sent.

15. **Notes will be given priority in publication.**

Change of address should be immediately intimated to the office.

No claims will be allowed for copies of Journal lost in the mail or otherwise, unless such claims are received within 90 days of the date of issue.

	Inland rates.	Foreign rates.	
		Sterling area	Dollar area
Cost of Single Issue	**Rs. 3**		
Annual Subscription	**,, 20 (for Fellows)**	**20**	**25**
	,, 24 (for Subscribers)	**28**	**32**
	,, 28 (Composite)	**34**	**40**

Inland Rates of Advertisement

In Ordinary Pages:
(Single insertion)

Full Page ...	... Rs. 40/-
Half Page ...	... ,, 25/-
Quarter Page ...	... ,, 15/-

In Cover Pages:		**In special positions:**	
Cover (Back) Full ...	Rs. 100/-	Page facing first reading matter ...	Rs. 70/-
,, ,, Half ...	,, 60/-	Page facing last page of reading matter...	,, 60/-
Second and Third Pages:			
Full Page ...	Rs. 70/-	Page facing inside front cover ...	,, 50/-
Half Page ...	,, 40/-	Page facing inside back cover ...	,, 50/
Quarter Page ...	,, 25/-		

Closing date for advertising materials: 7th of the previous month.

10% *Rebate allowed in cases of six consecutive full and half page insertions.*

All communications are to be addressed to:

The Hony. Secretary,
INDIAN CHEMICAL SOCIETY
92, Upper Circular Road. Calcutta-9.

WANTED

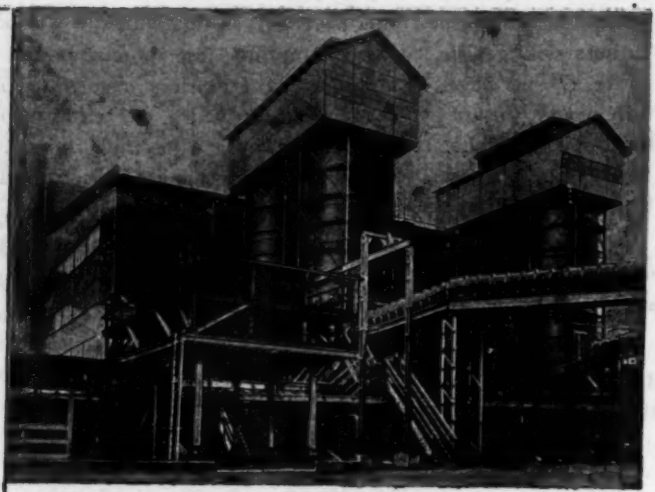
Back Complete Volumes or Single Issues of the Journals of All Subjects in any language

Please send complete details for immediate attention

to

TODAY & TOMORROW'S BOOK AGENCY

22B/2, Original Road, Karol Bagh, New Delhi-5



WE DESIGN
DELIVER &
ERECT

COMPLETE EQUIPMENT FOR H_2SO_4 PRODUCTION

WE SHALL OFFER TO YOU TECHNICAL UNITS
OF THE FOLLOWING OUTPUTS:

Raw material: SULPHUR	10 mt/24 hrs.	PYRITE	50 mt/24 hours
	25 mt/24 ,,		100 mt/24 ,,
	50 mt/24 ,,		150 mt/24 ,,

WE SHALL GUARANTEE A SUITABLE
AND UP-TO-DATE DESIGN AND ECONOMIC OPERATION

TECHNOEXPORT

Praha—Czechoslovakia

For informations please contact

TRADE REPRESENTATION OF CZECHOSLOVAK REPUBLIK,

BOMBAY BRANCH: KASTURI BUILDING, JAMSHEDJI TATA ROAD, BOMBAY.

CALCUTTA BRANCH: P-38, MISSION ROW EXTN., CALCUTTA.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

STUDIES ON THE ALKALOIDS OF *ALANGIUM LAMARCKII* THW.

By N. K. Basu and K. D. Gode

Five new alkaloids have been isolated from the bark of *Alangium lamarckii*. Different salts, estimation of functional groups, determination of molecular formulae and physical properties have been studied. Experiments on the structure of one of the isolated alkaloids, Base B_2, and the ultra-violet and the infra-red absorption spectra of the alkaloids and their degradation products have been described.

The provisional formulae of the alkaloids are: Base B_1 - $C_{19}H_{25}O_2N(OCH_3)(OH)_2$, m.p. 197-98°; Base B_2 - $C_{17}H_{31}O(NCH_3)(OCH_3)_2(OH)_3$, m. p. 119-20°; Base B_3 - $C_{16}H_{19}ON(OCH_3)(OH)_2$, m. p. 160-61°; Base B_4-$C_{17}H_{19}O_3N(OCH_3)_2(OH)_2$, m.p. 149-51° and Base B_5-$C_{19}H_{23}O_4N(OCH_3)_2(OH)_2$, m.p. 177-79°. The alkaloids are phenolic bases and contain condensed pyrrole nucleus.

Alangium lamarckii Thw. (N.O. Alanginaceae) is an Indian medicinal plant which has been widely used in India by physicians practising indigenous systems of medicine (Unani & Ayurvedic). Kirtikar and Basu ("Indian Medicinal Plants", L.M. Basu, Allahabad, 1935, Vol. II, p. 1237) have reviewed in detail the therapeutic use of the drug. The bark of the plant is used in leprosy, syphilis and various skin deseases. It is also diaphoretic, antipyretic, anthelmintic and is used in cases of dysentery. Pharmacological actions of crude alkaloidal sulphate were studied by Chopra ("Indian Medicinal Plants", Patna Univ., 1932, p. 272) and Raymond-Hamlet (*Compt. rend. Soc. Biol.*, 1941, **135**, 1011) studied pharmacological actions of an injectable extract.

Dymock ("Pharmacographia Indica", Education Society Press, Bombay, 1893, Vol. II, p. 164) reported the presence of an alkaloid which could not be crystallised. Chopra and Chowhan (*Ind. J. Med. Res.*, 1934, **21**, 507) isolated an alkaloid "Alangine" (m.p. 80-82°). Bhargava and Dutt (*Proc. Ind. Acad. Sci.*, 1942, **16A**, 328), while working on the seeds of the plant isolated a sterol "Alangol" ($C_{42}H_{84}O_7$, m.p. 296°). Manjunath *et al.* (*J. Mysore Univ.*, 1942, **3B**, 113) also isolated a sterol 'Alangol" from the seeds of the plant. Dutt and Parihar (*Proc. Ind. Acad. Sci.*, 1946, **23A**, 325) were successful in crystallising an alkaloid "Alanginine" (m.p. 205-208°) and prepared a number of salts of the base. The base has been shown to contain one methoxy group and one hydroxy group but no methylimino group. Basu *et al.* (*Ind. J. Pharm.*, 1950, **12**, 98) have isolated three more alkaloids, namely, "Akharkantine" (m.p. 146-48°), "Ankoline" (m.p. 110°, empirical formula $C_{17}H_{36}O_4N_2$) and "Lamarkine" ($C_{13}H_{12}O_6N_2$, m.p. 60-62°). The alkaloids were freely soluble in benzene and were isolated from the benzene-soluble fraction of the alkaloids. Singh and Tiwari (*Proc. Nat. Acad. Sci.*, 1948, **17A**, 1) reported the isolation of three bases, viz., "Alangium A" ($C_{21}H_{25}O_3N_2$, m.p. 219-20°), "Alangium B" (m.p. 105-107°) and "Alanginine C" (m.p. 245-47°). Subbaratnam and Siddiqui (*J. Sci. Ind. Res.*, 1956, **15B**, 432) isolated from the seed kernels of the plant a methylated alkaloid "Alamarckine" (m.p. 190-91°). From the U.V. and I.R. spectra

of the base the authors have proposed "$C_{24}H_{23}N(OCH_3)_3OH(NCH_3)$" as the provisional formula of the base. Presence of two double bonds has also been indicated.

As no exhaustive constitutional work appears to have been done on any of the alkaloids, reported so far, nor their pharmacological activity has been explored to any appreciable extent, it has been felt desirable that the drug should be worked upon further for the isolation of different alkaloids from *Alangium L.*, and to study their biological actions and chemical constitutions. The present work has been undertaken with this end in view and five hitherto-unreported alkaloids have been isolated. The method of isolation and purification are based on chromatographic separation. Different salts of the isolated bases have been prepared. Elementary analysis and functional group estimations have been carried out and the molecular formula determined. The alkaloid B_2 was obtained in greater yields and selected for the study of degradation products thereof. Selenium dehydrogenation, soda lime distillation, alkaline hydrolysis and oxidation of the base have been carried out. It has been possible to locate a condensed pyrrole nucleus in the degradation products. The ultraviolet absorption spectra of the alkaloids and their degradation products have been studied and infra-red absorption spectra of the alkaloids B_2 and B_5 have been examined, which support the analytical findings.

The biological properties of the bases have been studied and will be communicated elsewhere. The benzene-soluble bases, reported by previous workers, could not be isolated by the procedure adopted during the present investigation However, these will be dealt with in a future communication.

Experimental

Extraction and Preliminary Separation.—The powdered bark (20 kg.) of the plant (in No. 60 mesh) was moistened with 1% HCl and packed in glass percolators and extracted with 1% HCl by percolation process. The acid percolate (130 litres) was filtered and the filtrate made alkaline to litmus with a 10% aqueous solution of sodium carbonate. A voluminous chocolate-brown precipitate separated. The mixture was filtered under suction and the precipitate after being washed with little water was dried under vacuum and kept as precipitate "A" for further investigation. The filtrate from above was made distinctly acidic with H_2SO_4 (dil.) and the alkaloids were precipitated by Dragendorff's reagent. The deep orange-coloured precipitate was washed with water and dried in vacuo. The alkaloidal bismuth iodide was treated with dry acetone and the acetone solution decomposed with silver carbonate. The filtrate after removal of bismuth and silver by treatment with H_2S was marked "Solution B_1". The residual alkaloidal bismuth iodide, which was not soluble in acetone, was dissolved in alcohol and the filtrate decomposed with silver carbonate, and treated as before. This alcoholic solution was marked "Solution B_2".

Isolation of Alkaloid from "Solution B_1".—As no crystalline material was obtained from solution B_1, it was purified by redragendorffing and decomposing with silver carbonate as before. The residue was then dissolved in alcohol and passed over a column of alumina (55 × 3 cm, packed with 400 g. of B.D.H. alumina). The chro-

matogram obtained after developing with 95% alcohol was composed of an upper dark brown band (3 cm), followed by a lower deep yellow band (30 cm). The chromatogram was eluted with 95% alcohol and the lower yellow band was completely washed out from the column and received in the eluate fraction (300 c.c.). The dark brown band was found to contain non-alkaloidal resinous impurities, and was therefore rejected. The eluate was filtered and evaporated to dryness under vacuo, and the residue on prolonged refrigeration and crystallisation from acetone-ether mixture (1 : 3) afforded a pale yellow, amorphous mass, melting at 197-98°. The amorphous mass on repeated crystallisations from absolute alcohol yielded shining brown granules of the pure base, B_1 (5.5 g.), the melting point of which was found to be 197-98°.

Isolation of Alkaloid from "Solution B_2".—The solution B_2 containing alcohol-soluble alkaloids was also redragendorffed and decomposed with silver carbonate. It was then purified by passing over a column of alumina (55 × 3 cm, packed with 400 g. of B.D.H. alumina). On developing the chromatogram with alcohol, there appeared a dark brown band of 2.5 cm, followed by a lower pale yellow band of 21.5 cm. The column was eluted with 95% alcohol to wash away the lower pale yellow band. The eluate fraction (400 c.c.) was evaporated to dryness under reduced pressure ; the residue was taken up in methanol and the alkaloid was reprecipitated with ether. After repeating the precipitation of the alkaloid, finally the precipitated base was repeatedly crystallised from absolute ethanol at 0° (in refrigerator). This yielded another pure base, B_2 (7.5 g.), m.p. 119-20°.

Isolation of Alkaloids from the Precipitate "A".—The precipitate "A" containing crude alkaloids, precipitated by sodium carbonate, was digested with hot alcohol and filtered. The alcohol-insoluble portion was labelled "A_1" and the alcoholic filtrate, "A_2", was poured in a thin stream into a large volume of ethyl acetate, and the ethyl acetate-insoluble fraction was separated by filtration and labelled "A_3". The ethyl acetate filtrate "E" was concentrated and fractionally precipitated with water into two water-insoluble fractions, "E_1" and "E_2", and the filtrate after separation of fraction "E_2" was evaporated ; the residue was labelled "E_3".

Precipitate "A_1" obtained was not sufficient and therefore no attempts for crystallisation could be made.

Precipitate "E_1" was dissolved in alcohol (50 c.c.) and the solution was poured in a large excess of water whereupon the precipitate reappeared. This process was repeated several times to remove water-soluble impurities, and a brown amorphous residue was obtained. It was digested with hot methyl alcohol and the small insoluble portion was rejected. The menthanolic solution was treated with animal charcoal and finally the filtrate on refrigeration over a long period yielded a brown crystalline material. It was repeatedly crystallised from methanol to yield a new base, "B_3", m.p. 160-61°.

Precipitate "E_3" was not considered sufficient for further work.

Treatment of Residue "E_3".—The residue was dissolved in 95% alcohol and ether was added to it in small portions. A dark brown amorphous precipitate separated, leaving the supernatant liquid deep brown in colour. The precipitate was washed with ether. The decantate and the ethereal washings gave on evaporation a negligible amount of

a residue. Several attempts to crystallise the ether-insoluble fraction from different solvents did not succeed. It was then dissolved in alcohol and acetone mixture (1 : 1) and passed through 420 g. of alumina, packed in a column (55 × 3 cm). The chromatogram was first developed with acetone and then with a mixture of acetone and alcohol (3 : 1). At this stage the elution was terminated and the chromatogram was composed of the following bands from its upper end to lower end :—(1) Dark brown band, 2.5 cm. (2) Pale brown band, 4.5 cm. (3) Yellowish brown band, 4 cm. (4) Light orange-red band, 6 cm. (5) Pale yellow band, 18 cm. (6) White band, 14 cm. (7) Deep yellow band, 2 mm. The bands were separated from the column by means of a spatula and each one of them was digested with hot alcohol and the alcoholic extracts were evaporated. The residue obtained from the 4th orange-red band appeared to be more pure and free from resinous matter, while those obtained from the other bands were resinous and also very small in quantity, and therefore could not be worked further. The residue from the 4th band was redissolved in acetone and passed over a column of alumina (20 × 3 cm), the adsorbent was removed and digested with alcohol. The alcoholic solution on prolonged refrigeration deposited an orange-red microcrystalline precipitate, which, on repeated crystallisation from alcohol-ether mixture, yielded a pure new crystalline base, "B_4", m.p. 149-50°.

Treatment of Precipitate "A_3".—The precipitate containing ethyl acetate-insoluble fraction of the alkaloids was extracted with alcohol and filtered. A little insoluble residue was rejected. The alcoholic filtrate was concentrated (150 c.c.) and poured in distilled water (800 c.c.) whereupon some precipitate appeared which was separated by filtration. The filtrate was evaporated to dryness in a vacuum desiccator ; the residue (25.5 g.) was dissolved in alcohol (20 c.c.) and the solution was added to 200 c.c. of acetone whereupon a dark brown precipitate separated. The supernatant liquid was decanted and evaporated to dryness in vacuo. The residue (23.5 g.) was dissolved in 100 c.c. of acetone and alcohol mixture (1 : 1) and passed through 450 g. of alumina, packed in a column (60 × 3 cm). The chromatogram was developed with acetone till 600 c.c. of eluate was collected ; the development was satisfactory. The chromatogram was composed of the following bands :—(1) Dark brown band, 2 cm. (2) Pale brown band, 13 cm. (3) Deep orange-red band, 31 cm. (4) Pale yellow band, 10 cm. (5) Deep yellow band, 2 cm. The fifth deep yellow band was washed away in the acetone eluate, which on evaporation under vacuo yielded a resinous dark brown residue. It was not worked further. The column was partially dried under suction and the different bands were separated by means of a long glass spatula. Each of them was extracted with hot alcohol and the alcoholic extracts after filtration and evaporation under vacuo yielded residues from the respective bands. Out of all the residues, the one obtained from the third deep orange-red band was more in quantity (11.2 g.) and appeared to be free from associated resinous impurities and, therefore this was taken for purification; the other residues were not worked further.

The residue (11.2 g.), obtained above, was dissolved in alcohol and again passed through a column of alumina (45 × 3 cm). After satisfactory development of the chromatogram with acetone-alcohol mixture (1 : 1), the column was dried and the adsorbent removed. The alkaloid was extracted from the adsorbent with hot alcohol and the

alcoholic extract (2.5 litres) was evaporated to dryness in vacuo. Attempts to crystallise the base from this residue by fractional crystallisation using different solvents did not meet with success. Therefore, a little quantity of the residue was dissolved in 0.5% H_2SO_4 and the base was precipitated with Dragendorff's reagent and decomposed with silver carbonate as usual. But it was found that the base was decomposed in this process. In another trial the base was precipitated as insoluble reineckate and decomposed with silver carbonate. This process proved successful. Therefore, the remainder of the alkaloidal residue was extracted with 0.5% H_2SO_4 and precipitated with a saturated aqueous solution of ammonium reineckate ; the insoluble alkaloidal reineckate was separated by filtration. The precipitate was dissolved in acetone and decomposed with sufficient silver carbonate till a portion of the mixture on filtration gave negative test with silver nitrate solution. The mixture was filtered and the filtrate was concentrated in vacuo and refrigerated for a week whereupon a deep orange-red crystalline mass separated. On repeated crystallisations from absolute alcohol, it yielded pure alkaloid "B_5", m.p. 177-79°.

CHART I

Scheme for separation of alkaloids.

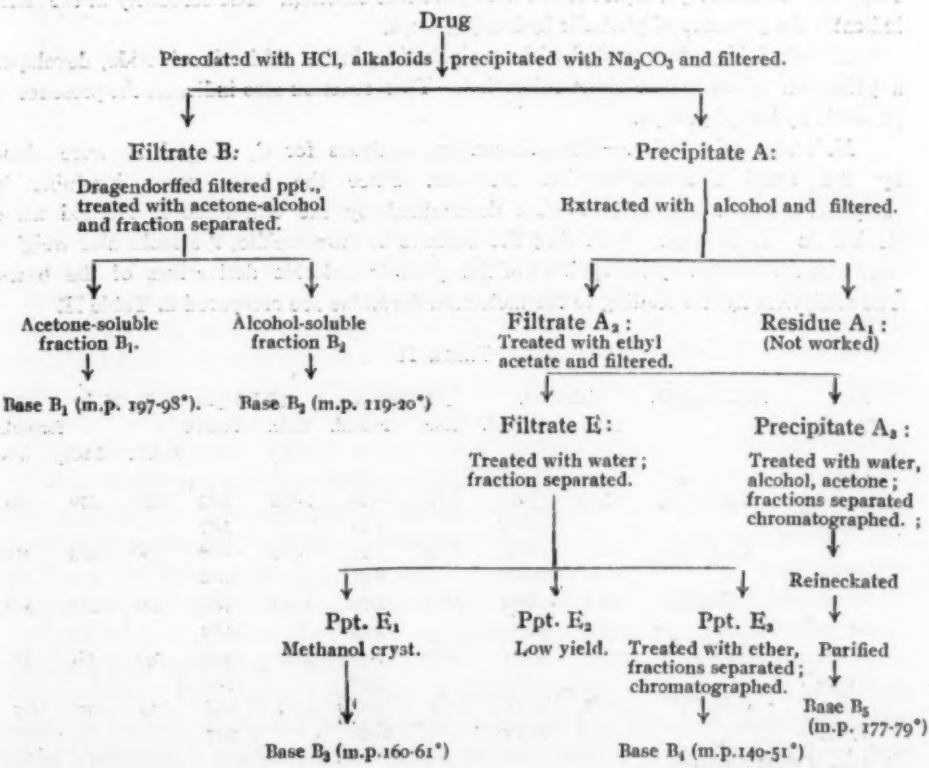


TABLE I

Melting points of the salts of alkaloids.

Salts.	Base B_1.	Base B_2.	Base B_3.	Base B_4.	Base B_5.
Hydrochloride	228-29°	188°	181°	199°	208°
Picrate	166-67°	139° (decomp.)	143-45° (decomp.)	142°	91°
Picrolonate	205-10°	164°	243° (,,)	175°	199°
Platinichloride	Darkens at 235° and melts at 272° (decomp.)	Darkens at 207° and melts at 215° (decomp.)	Darkens at 191° and melts at 232° (decomp.)	205° (decomp.)	249° (decomp.)
Aurichloride	Darkens at 220°; melts at 235° (decomp.)	Darkens at 195°; 292° (decomp.)		182° (,,)	151° (,,)
Bismuth iodide	194-95° (decomp.)	215° ,,	265° ,,	175° ,,	225° ,,
Hydro-iodide	213-15° ,,	189° ,,	227° ,,	174° ,,	194° ,,
Reineckate	Charred at 249°	Darkens at 235° and melts at 266° (decomp.).	Charred at 245°	Charred at 248°	Charred at 305°

Solubility of the Alkaloids.—All the alkaloids were found to be freely soluble in ethyl alcohol and in 5% aqueous sodium hydroxide solution. The solubility in the latter indicates the presence of phenolic hydroxy groups.

The alkaloids, when treated with an alcoholic solution of ferric chloride, developed a yellowish green to pale violet coloration. This reaction also indicates the presence of phenolic hydroxyl groups.

Molecular Formulae.—The elementary analyses for C, H and N were done by the usual micro-combustion methods. Since the bases were insoluble in camphor, the molecular weights were determined by the ebullioscopic method using alcohol as the solvent. Assuming the bases to be mono-acidic, the molecular weights were also determined by the ignition of the platinic chloride derivatives of the bases. The analytical figures leading to the molecular formulae are compared in Table II.

TABLE II

Base with m.p.	Mol. formula.	%Carbon. Calc.	%Carbon. Found.	%Hydrogen. Calc.	%Hydrogen. Found.	%Nitrogen. Calc.	%Nitrogen. Found.	M. W. by * B.P.	M. W. by $PtCl_4$.	Calc. formulae wts.
B_1 (197-98°)	$C_{20}H_{31}O_5N$	65.75	65.79 65.83	8.494	8.51 8.52	3.835	3.83 3.87	356	370	365
B_2 (119-20°)	$C_{27}H_{43}O_6N$	66 53	66.99 66.82	8.831	8.97 8.91	2.935	2.93 2.86	496	483	477
B_3 (160-61°)	$C_{17}H_{24}O_4N$	66.67	66.42 66.49	7.843	7.79 7.93	4.575	4.63 4.62	302	310	306
B_4 (149-51°)	$C_{19}H_{27}O_7N$	59.84	59.75 59.84	7.087	7.10 7.08	3 675	3.65 3.67	391	381	381
B_5 (177-79°)	$C_{21}H_{31}O_8N$	59.29	59.21 59.32	7.295	7.28 7.25	3.294	3.28 3.27	429	430	425

* Mean of three readings.

† Mean of two readings.

TABLE III

Hydrochlorides of the alkalotids (analysis by combustion).

Base.	Mol. formula.	Calc.				Found.			
		%C.	%H.	%N.	%Cl.	%C.	%H.	%N.	%Cl.
B_1	$C_{20}H_{32}O_8NCl$	59.78	7.97	3.48	8.84	59 43	7.84	3 46	8.86
B_2	$C_{27}H_{44}O_6NCl$	63.10	8.57	2.72	6.91	63.25	8.59	2.73	6.95
B_3	$C_{17}H_{25}O_4NCl$	59.57	7.30	4.12	10.36	59.22	7.28	4.13	10.45
B_4	$C_{19}H_{28}O_7NCl$	54.63	6.70	3.35	8.50	54 78	6.73	3.39	8.67
B_5	$C_{21}H_{32}O_8NCl$	54.61	6.93	3.03	7.60	54.72	6.97	3.07	7.55

Estimation of Functional Groups.—Hydroxy groups were estimated by Peterson's method (*Ind. Eng. Chem. Anal. Ed.*, 1943, **15**, 227). Estimation of methoxyl groups was carried out by Zeisel's method and N.Me group was estimated by Herzig and Meyer's method. The number of functional groups in different alkaloids are shown in Table IV.

TABLE IV

Base.	Mol. formula.	No. of OH groups.	No. of OMe groups.	No. of N.Me groups.
B_1	$C_{20}H_{31}O_8N$	2	1	Nil
B_2	$C_{27}H_{43}O_6N$	3	2	1
B_3	$C_{17}H_{24}O_4N$	2	1	Nil
B_4	$C_{19}H_{27}O_7N$	2	2	Nil
B_5	$C_{21}H_{31}O_8N$	2	2	Nil

Constitutional Investigations

Out of the five alkaloids, the base B_2 ($C_{27}H_{43}O_6N$, m.p. 119-20°) was obtained in sufficient yields, and it was subjected to constitutional studies. It has been shown that the base B_2 contains two OMe groups, three OH groups and one N.Me group. Solution of the base in acetone did not develop any coloration with a solution of sodium nitroprusside (Rimini's test). Similarly, the alcoholic solution of the base to which a freshly prepared solution of acetaldehyde was added also showed no coloration with sodium nitroprusside (Simon's test). These reactions indicate that the nitrogen atom is not primary or secondary, but of tertiary nature, having a methyl group attached to it.

Selenium Dehydrogenation.—A mixture of the base B_2 (2 g.) and selenium powder (6 g.) was heated in a current of dry hydrogen and the receiving bulbs were surrounded with crushed ice. The temperature was kept at 280° and later raised to 340°. Four fractions were collected: (1) basic portion contained in the alcoholic hydrochloric acid trap bulbs, (2) basic aqueous yellow liquid in the receiving bulb, (3) water-insoluble basic substance collected in the side tube and (4) selenium melt in the distilling bulb.

Fraction 1: The acid liquid on evaporation left a white crystalline deposit which was found to be ammonium chloride.

Fraction 2: This yellow liquid was alkaline to litmus and emitted piperidine-like odour. It may be mentioned here that the odour of pyrrolidine is quite resembling that of piperidine. Due to very low yield it was not possible to dry the liquid and note

its boiling point. Therefore its picrate was prepared by adding an aqueous saturated solution of picric acid and warming. The picrate crystallised on concentration and refrigeration, and after being washed with little water, the crystals melted at 112-13°. The melting points of the picrates of pyrrolidine, pyrrole and piperidine are 112°, 69° and 152° respectively.

Fraction 3 : It could not be worked further for any conclusive results.

Fraction 4 : Selenium-melt in the distilling bulb was extracted with ether and then with hot alcohol. The alcoholic extract was evaporated and the residue was taken up in ether and the combined ethereal extract of the melt was shaken with 5% H_2SO_4 to remove any basic fraction. After washing the ethereal layer with distilled water, it was dried over anhydrous sodium sulphate and concentrated. On refrigeration overnight a few white crystals separated which on centrifuging and subsequent crystallisation from absolute alcohol yielded 6 mg. of the crystalline material. It melted at 134-35° (micro-melting). The ultraviolet absorption of the solution of this substance in alcohol was taken using Unicam S. P. 500 spectrophotometer, and since it showed an absorption maximum at $\lambda = 280$ mμ (Fig.1) a carbonyl group was suspected. This was confirmed as the substance gave yellow precipitate with 2 : 4-dinitrophenylhydrazine reagent. No further work on this substance could be done.

Soda-lime Distillation.—Soda-lime distillation in a current of dry nitrogen evolved white fumes which gave positive pine-splinter reaction, indicating pyrrole type of compounds. The aqueous liquid collected in the receiving bulb was smelling like pyrrolidine. It gave positive isatin reaction and a red coloration with *p*-dimethylamino-benzaldehyde solution, indicating pyrrole or indole type of compounds. The remainder of the distillate was made alkaline with dilute NaOH solution and an 1% aqueous solution of sodium nitroprusside was added when it acquired a brownish colour. It was acidified with acetic acid and the reddish brown colour was extracted with chloroform, indicating presence of a pyrrole body. This test recommended by Herzfeld (Allen's Commercial Organic Analysis, J. & A. Churchill, London, 1938, Vol. V, pp. 648 651) distinguishes pyrrole from indole, which under similar conditions shows violet-blue colour which is not extracted with chloroform.

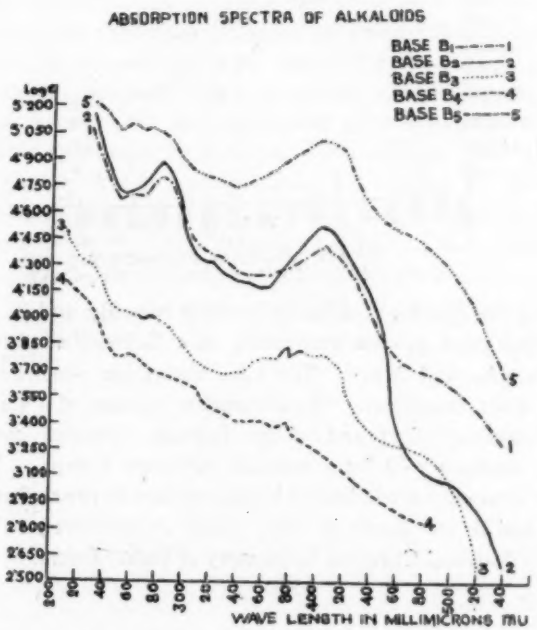
Alkaline Hydrolysis.—The base B_2 (1.5 g.) was refluxed with 10% alcoholic KOH (50 c.c.) for 6 hours. The liquid was filtered, acidified with H_2SO_4 (dil.) and extracted with ether in a liquid-liquid continuous extraction apparatus. The ether extract containing the non-basic fraction was dried and the solvent removed. The residue was dissolved in absolute alcohol (10 c.c.) and passed over a column of alumina and was eluted with alcohol. The eluate yielded white needle-shaped crystals, m.p. 113-14°, which did not react with 2 : 4-dinitrophenylhydrazine, showing absence of carbonyl group. Due to low yields only its U. V. absorption spectra could only be taken. For working out the basic fraction the aqueous liquid was rendered alkaline and shaken with chloroform. On evaporation no crystalline material could be obtained, but a picrate melting 147-48° could be prepared.

Oxidation.—The base B_2 (2 g.) was dissolved in dry acetone and carefully oxidised with $KMnO_4$ (2.5 g.) at room temperature for 14 days. The mixture was filtered and the residue extracted with dry acetone. The acetone extract was evaporated in vacuo

and taken up in chloroform and later in alcohol and purified through an alumina column. From the eluate a needle-shaped colorless crystalline mass melting at 109° was obtained. Its solution in neutral alcohol was acidic to litmus and liberated iodine from a mixture of potassium iodide and iodate. Since the quantity was too small for any analytical work, it was mixed with soda-lime and heated over a microburner. The vapours gave positive pine splinter test.

Spectrophotometric Studies.—The alkaloids were dissolved in alcohol and absorption measurements were taken between λ 210 and λ 540 mμ on a Unicum spectrophotometer (S.P. 500). The absorption spectra of the alkaloids are shown in Fig. 1. The spectra of B_1 and B_2 show absorption maxima at λ 283 mμ and λ 405 mμ. Both the spectra are similar. The spectrum of alkaloid B_5 also resembles in some respects. There is a general absorption below λ 230 mμ, which may be due to hydroxy groups. The spectra of alkaloids B_3 and B_4 are similar. In general, the U. V. absorption spectra of the alkaloids speak of their similarity in chromophoric functions.

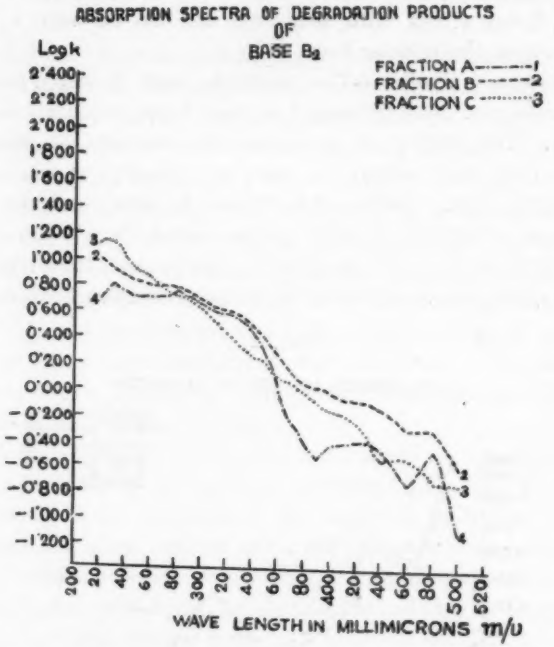
FIG. 1



Absorption Spectra of Degradation Products.—The fractions taken for measurements were: (*a*) non-basic substance (m.p. 134-35°) from selenium dehydrogenation of base B_2, (*b*) non-basic substance (m.p. 13-114°) from alkaline hydrolysis of base B_3 and (*c*) basic water-insoluble substance from soda-lime distillation of base B_2. The absorption spectra of the alcoholic solutions of the above fractions were taken between λ 220 and λ 500 mμ. The absorptions are represented in Fig. 2. The spectrum of fraction A shows absorption maxima at λ 230, λ 280 and λ 480 mμ. It appears to be a complex

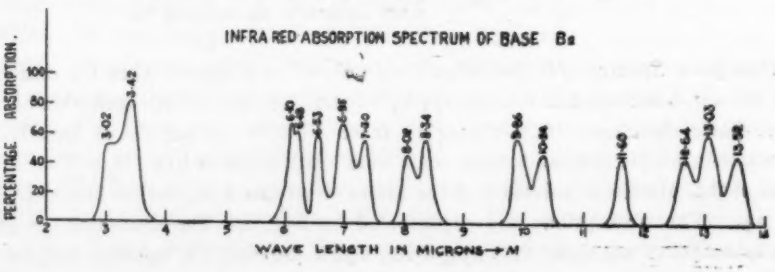
substance. The peak at λ 280 mμ may be attributed to carbonyl group. The spectra of fractions B and C do not show any characteristic peaks.

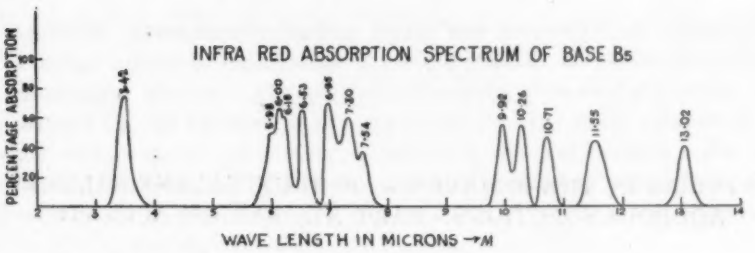
FIG. 2



Infra-red Absorption Spectra of Alkaloids.—Only base B_2 and B_5 were selected for the I.R spectra. Their solid spectra were taken on a Grubb-Parson spectrometer with NaCl prism, between λ 2 and λ 14μ. The I.R. absorption spectra of base B_2 and B_5 show similarity in their structures. The absorption maxima at λ 3.42μ may be due to alkyl groups. Maxima at λ 6.53 and λ 6.95μ indicate potential carbonyl functions. Absorption in the region λ 7 - λ 8.5 μ indicate methoxyl groups. Unsaturation and complex polycyclic structures are indicated by absorptions in the region λ9 - λ 13μ. The I.R. spectra of B_2 and B_5 are shown in Figs. 3 and 4 respectively. The I.R. records were obtained at the National Chemical Laboratory of India, Poona.

FIG. 3





CONCLUSION

Qualitative tests, solubility and analytical data of the alkaloids indicate that all the alkaloids are phenolic bases containing methoxy groups. The alkaloid B_2 m.p. 119-20°) on selenium dehydrogenation yields a ketonic body, showing positive reaction with 2 : 4-dinitrophenylhydrazine reagent. The pure base, however, does not exhibit positive reaction with this reagent. The picrate of the basic substance from selenium dehydrogenation resembles pyrrolidine picrate, but its exact identity could not be established. Soda-lime distillation was attempted to locate the heterocyclic nucleus present in the molecule. But this could reveal only a pyrrole or a condensed pyrrole nucleus. Oxidation with $KMnO_4$ afforded an acid containing pyrrole nucleus, and alkaline hydrolysis yielded a non-basic substance (m.p. 113-14°) and a basic picrate (m.p. 147-48°), which could not throw much light on constitution. U.V. and I. R. absorption spectra show similarity in structural make up of the alkaloids. But no definite conclusion regarding the nucleus could be derived from the spectra. In fact, it is necessary to isolate one of the products of degradation in good yield for further work.

DEPARTMENT OF PHARMACEUTICS,
BANARAS HINDU UNIVERSITY,
BANARAS.

Received March 25, 1957.

[Jour. Indian Chem. Soc., Vol 34, No. 9, 1957]

STUDIES IN THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTIONS. PART XI. BARIUM ACETATE

By B. Nayak and B. Prasad

From the study of the cells of the type

$Hg/Hg_2Ac_2\ BaAc_2(C_1)$/saturated $NH_4NO_3/BaAc_2(C_2)\ Hg_2\ Ac_2/Hg$

and the solubility of barium iodate in potassium nitrate and potassium acetate solutions, the dissociation of barium acetate in its aqueous solutions has been determined. Barium acetate has been found to be completely dissociated in its aqueous solutions at least up to a concentration of 0.1 *M*.

In an earlier communication by Prasad *et al.* (this *Journal*, 1953, **30**, 633), barium acetate was assumed to be completely dissociated in its aqueous solutions up to 0.1*M*. Since barium ion forms complexes with some organic acid anions, the present investigation has been undertaken to test the validity of the earlier assumption.

The cells of the type,

$$Hg/Hg_2Ac_2\ BaAc_2(C_1)/\text{saturated}\ NH_4NO_3/BaAc_2(C_2)\ Hg_2Ac_2/Hg$$

(where '*C*' indicates concentration of barium acetate in g. mol. per litre), were studied and the solubility of barium iodate was determined separately in potassium nitrate and potassium acetate solutions of varying concentrations.

Experimental

Barium acetate used was of E. Merck's reagent quality and was recrystallised before use. The stock solution of the salt was prepared in double distilled water and its exact concentration was determined gravimetrically as barium sulphate. The other solutions were prepared from the stock solution by dilution. Pure distilled mercury and chemically precipitated mercurous acetate were used for preparing the electrodes. The cell vessels and the bridge were of the type previously used (this *Journal*, 1951, **28**, 683).

The E.M.F. was measured with the help of a K-type Leeds-Northrup potentiometer at $35° \pm 0.02°$ in an electrically regulated air thermostat. Duplicate experiments were performed for each combination of half cells and the duplicates agreed within 0.2 mv. The half cells having the same composition were checked against each other. The E.M.F. produced by such a combination was mostly less than 0.1 mv. In cases where it exceeded this limit, the half cells concerned were rejected.

For solubility measurements barium iodate was prepared by precipitation from a solution of barium acetate by the addition of a dilute solution of potassium iodate with constant mechanical stirring. The precipitated sample, after careful washing and drying, was analysed (% Ba expected 27.19 ; found 27.17). The stock solution of potas sium acetate was prepared by mixing calculated amounts of standard acetic acid and potassium hydroxide solutions. The stock solution of potassium nitrate was prepared by weighing the salt. The 0.0, 0.02, 0.04, 0.06, 0.08 and 0.1 molar solutions were prepared by diluting the stock solution.

The solutions containing an excess of barium iodate were shaken in glass-stoppered bottles for about five days on a mechanical shaker and then were allowed to stand for about three days inside an air thermostat at 35°. These periods were found sufficient for the attainment of equilibrium. The solubility was determined by estimating the amount of iodate in the solution phase by titrating with a standard 0.009535N thiosulphate solution.

TABLE I

C_1.	C_2.	E.M.F. (obs.)	E.M.F. (calc.)	C_1.	C_2.	E.M.F. (obs.)	E.M.F. (calc.)
0.01	0.04	0.03422	0.03380	0.02	0 10	0.03900	0.03856
0.01	0.06	0.04322	0.04350	0.04	0.06	0.00920	0 00970
0.01	0.08	0.05087	0.05030	0.04	0.08	0.01682	0 01650
0.01	0.10	0.05535	0.05560	0.04	0.10	0.02250	0.02180
0.02	0.04	0.01580	0.01677	0.06	0.08	0.00675	0 00680
0.02	0.06	0.02630	0.02646	0.06	0.10	0.04322	0 04350
0.02	0.08	0.03250	0.03331	0.08	0.10	0.00520	0.00535

ISCUSSION

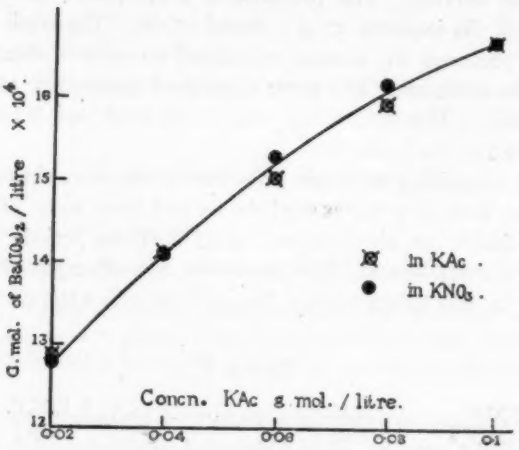
The E.M.F's of the cells of the type used above at 35° are shown in the table in all cases except for the combination 0.01M, 0.02M as reproducible readings could not be obtained in this case. The E.M.F. of the cells may also be calculated from the equation

$$E = \frac{RT}{F} \ln \frac{C_1}{C_2} \frac{f_1}{f_2}$$

where C_1 and C_2 and f_1 and f_2 are respectively the concentrations and the activity coefficients of acetate ions in the two solutions. If barium acetate is assumed to be completely dissociated, the concentration of the acetate ion will be twice the molar concentration of barium acetate. The activity coefficient of acetate ion may be assumed to be the same as that of the chloride ion at the same ionic strength. The calculated E.M.F's on the basis of the above assumption are shown in the last column of the table. It is found that the calculated and the observed E.M.F's agree within 1 mv in all cases where reproducible readings are available. This clearly indicates that in the

case of barium acetate the dissociation is almost complete within the range of concentrations studied.

FIG. 1



Conc. of KNO_3 *(g. mol./litre)*

In dilute solutions of barium nitrate we expect complete dissociation on account of the structure of the nitrate ion. If dissociation is incomplete in the case of barium acetate, the solubility of barium iodate in the same concentrations (having the same ionic strength) of potassium nitrate and potassium acetate would become different. The figure given shows that there is hardly ny such difference. This further supports the above view that barium acetate is almost completely dissociated in its aqueous solutions up to the concentration of 0.1 *M*.

MAYURBHANJ CHEMICAL LABORATORY,
RAVENSHAW COLLEGE, CUTTACK.

Received April 25, 1957.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

THE KINETICS OF THE FERRIC THIOSULPHATE REACTION. PART I

By D. Patnaik, C. Nanda and K. Bakshi

From the mechanism involving the two intermediates $FeS_2O_3^+$ and $Fe(S_2O_3)_2^-$, suggested for the ferric thiosulphate reaction (Patnaik and Mahapatra, *Curr. Sci.*, 1955, **24**, 195), kinetic equations have been derived for the initial and maximum rates of decay which have been measured spectrophotometrically at different ionic strengths for varying concentrations of ferric and thiosulphate ions. The initial rate varies as the first power of the concentrations of the ferric ion and the square of the concentration of the thiosulphate ion. On the other hand, the maximum rate varies as the square of the concentration of the coloured complex $FeS_2O_3^+$. These observations conform to the kinetic equations derived for the rates from the proposed mechanism, the various steps of which consist of bimolecular reactions between oppositely charged ions and ion-pairs. The decrease in rates, both initial and maximum, with the increase in ionic strength substantiates the fact that the rate-controlling stages are reactions involving oppositely charged ions.

The over-all ferric thiosulphate reaction is represented by

$$2Fe^{3+} + 2S_2O_3^{2-} = 2Fe^{2+} + S_4O_6^{2-} \qquad \ldots (1)$$

A labile coloured complex is formed when a solution of thiosulphate is added to that of a ferric salt. This coloured complex has been shown to possess the formula $FeS_2O_3^+$ (Das, Nanda and Patnaik, this *Journal*, 1956, **33**, 459). The decay curve of this complex $FeS_2O_3^+$ is of S-shape, which suggests the autocatalytic nature of the decay. In order to explain this autocatalytic nature, the following mechanism was suggested (Patnaik and Mahapatra, *Curr. Sci.*, 1955, **24**, 195).

$$Fe^{3+} + S_2O_3^{2-} \rightleftharpoons FeS_2O_3^+$$

$$FeS_2O_3^+ + S_2O_3^{2-} \rightleftharpoons Fe(S_2O_3)_2^-$$

$$Fe(S_2O_3)_2^- + FeS_2O_3^+ \rightarrow 2Fe^{2+} + S_4O_6^{2-} + S_2O_3^{2-}$$

$$Fe(S_2O_3)_2^- + Fe^{3+} \rightarrow 2Fe^{2+} + S_4O_6^{2-}$$

The mechanism put forward above can be written in the following set of equations:

$$k_1 : A + B \longrightarrow AB \qquad \ldots (i)$$

$$k_2 : AB + B \longrightarrow AB_2 \qquad \ldots (ii)$$

$$k_3 : AB_2 + AB \longrightarrow \text{products} + B \qquad \ldots (iii)$$

$$k_4 : AB_2 + A \longrightarrow \text{products} \qquad \ldots (iv)$$

$$k_5 : AB_2 \longrightarrow AB + B \qquad \ldots (v)$$

$$k_6 : AB \dashrightarrow A + B \qquad \ldots (vi)$$

where $A = Fe^{3+}$; $B = S_2O_3^{2-}$; $AB = FeS_2O_3^+$; $AB_2 = Fe(S_2O_3)_2^-$, products $= 2Fe^{2+} + S_4O_6^{2-}$ and k_1, k_2, etc. are velocity constants of the various reactions.

So $$\frac{-d(AB)}{dt} = k_1(A)(B) + k_2(AB)(B) + k_3(AB_2)(AB) + k_5(AB_2) + k_6(AB)$$

Reactions (*i*) and (*vi*) have been shown by Schmid (*Z. physikal Chem.*, 1930, 148, 321) to be extremely rapid and therefore k_1 (A)(B) = k_6(AB) is maintained throughout. And so

$$\frac{-d(AB)}{dt} = k_2 (AB) (B) + k_3 (AB_2) (AB) - k_5 (AB_2) \quad \ldots (2)$$

When the rate attains a maximum value at the quasi-stationary state, the rate of formation of the intermediate AB_2 must be equal to its rate of disappearance. Hence,

$$k_2 (AB) (B) = k_3(AB_2) (AB) + k_4 (AB_2) (A) + k_5 (AB_2).$$

Hence, $$(AB_2) = \frac{k_2 (AB) (B)}{k_3(AB) + k_4(A) + k_5}.$$

Substituting this value of (AB_2) in equation (2), we get

$$\frac{-d (AB)}{dt\ (max)} = k_2 (AB)^2 \left[\frac{2k_3 (B) + k_4 \frac{(A)(B)}{(AB)}}{k_3(AB) + k_4(A) + k_5} \right]$$

$$= k_2 (AB)^2 \left[\frac{2k_3 (B) + k_4 \frac{k_6}{k_1}}{k_3 (AB) + k_4 (A) + k_5} \right]$$

$$= \frac{k_2 k_4 k_6}{k_1} .(AB)^2 \left[\frac{\frac{2k_1 k_3}{k_4 k_6}(B) + 1}{k_3(AB) + k_4(A) + k_5} \right] \quad \ldots (3)$$

In equations (*iii*) and (*iv*), AB_2 is involved and, further, (AB) is dependent on (A). It would therefore be quite in order to substitute $k_3(AB) + k_4 (A)$ by $k'_3 (AB)$, the physical implication being that the rate represented by (*iv*) bears a constant relationship with that represented by (*iii*). So equation (3) reduces to

$$\frac{-d (AB)}{dt\ (max)} = \frac{k_2 k_4 k_6}{k_1} . (AB)^2 \left[\frac{\frac{2k_1 k_3 (B)}{k_4 k_6} + 1}{k'_3 (AB) + k_5} \right]$$

$$= \frac{k_2 k_4 k_6}{k_1 k_5} . (AB)^2 \left[\frac{\frac{2k_1 k_3}{k_4 k_6} + 1}{\frac{k'_3 (AB)}{k_5} + 1} \right] = k (AB)^2 \left[\frac{1 + m (B)}{1 + n(AB)} \right]$$

It can be seen from Table III that the ratio of the initial concentration of B to that of AB varies from 4 to 8. So, if the value of n be on the average 6 times that of m, then

$$\frac{1 + m\,(B)}{1 + n\,(AB)} \approx 1,$$

and hence, $$\frac{-d(AB)}{dt}\,(\max) = k\,(AB)^2.$$

In other words

$$(AB)^2 \,/\, \frac{-d(AB)}{dt}\,(\max) = \text{constant} \quad \ldots \quad \ldots \quad (4)$$

However, in the initial stage, $(AB_2) = 0$ and so the rate of decay becomes

$$\frac{-d\,(AB)}{dt}\,(\text{initial}) = k_2\,(AB)\,(B) = \frac{k_1 k_2}{k_5}.\,(A)\,(B)^2 = k'\,(A)(B)^2.$$

In other words

$$(A)\,(B)^2 \,/\, \frac{-d\,(AB)}{dt}\,(\text{initial}) = \text{constant} \quad \ldots \quad (5)$$

EXPERIMENTAL

The experimental details have been described previously (Das *et al.*, *loc. cit.*). The ionic strength was maintained by addition of sodium perchlorate. The H^+-ion concentration was maintained constant at 0.05 M and the working temperature was $25^\circ \pm 0.1^\circ$. In Tables I and II the actual concentrations of Fe^{3+} (A) and $S_2O_3^{2-}$ (B) have been recorded in moles per litre. The effective concentrations have been shown in Table III. Also in Tables I and II, log I has been noted against time, log I_0 being always 2 for 100% transmission. The values of log I recorded against zero-time were obtained by extrapolation of the log I – time curve.

The rates of decay, both initial and maximum, have been calculated as follows. Let C_1 and C_2 be the concentrations of $FeS_2O_3^+$ at times t_1 and t_2 respectively.

Then the rate $$= \frac{C_1 - C_2}{t_2 - t_1} = \frac{\log\,(I_0/I_{t_1}) - \log\,(I_0/I_{t_2})}{\epsilon.\ c.\ d.\ (t_2 - t_1)}.$$

Since $\epsilon.\ c.\ d. = \log\,(I_0/I)$ (Bears law), where ϵ = extinction coefficient and d = thickness of the liquid layer.

The mean concentration of $FeS_2O_3^+$ is represented by

$$\frac{C_1 + C_2}{2} = \frac{\log\left(\frac{I_0}{I_{t_1}}\right) + \log\left(\frac{I_0}{I_{t_2}}\right)}{\epsilon.\ d.} = \frac{2 - \frac{1}{2}\,(\log I_{t_1} + \log I_{t_2})}{\epsilon.\ d.}$$

since I_0 is always 2 for 100% incident transmission.

All measurements were made at the wave-length of 5000 Å.

TABLE I

$\mu = 0.12$.

Time.	Log I at compositions (A)=10 (B)=5	(A)=5 (B)=10	(A)=5 (B)=5	(A)=5 (B)=7.5	Time.	Log I at compositions (A)=10 (B)=5	(A)=5 (B)=10	(A)=5 (B)=5	(A)=5.5 (B)=7.5
0 sec.	1.061	0.966	1.390	1.157	55 sec.	1.851	1.762	1.780	1.778
5	1.079	1.000	1.398	1.176	60	1.892	1.792	1.810	1.808
10	1.114	1.070	1.415	1.211	65	1.924	1.823	1.834	1.834
15	1.176	1.154	1.443	1.273	70	1.948	1.840	1.856	1.853
20	1.255	1.249	1.477	1.342	75	1.964	1.854	1.875	1.869
25	1.357	1.347	1.519	1.419	80	1.973	1.869	1.889	1.884
30	1.455	1.447	1.565	1.505	85	1.982	1.885	1.903	1.896
35	1.562	1.535	1.615	1.574	90	1.986	1.895	1.914	1.906
40	1.648	1.608	1.663	1.639	95	...	1.905	1.920	1.914
45	1.738	1.672	1.708	1.697	100	...	1.911	1.929	1.920
50	1.796	1.720	1.748	1.740					

TABLE II

Time.	Log I at compositions (A)=10 (B)=10	(A)=10 (B)=5	(A)=5 (B)=10	(A)=5 (B)=5	Log I at compositions (A)=10 (B)=10	(A)=10 (B)=5	(A)=5 (B)=10	(A)=5 (B)=5
			$\mu = 0.25$.				$\mu = 0.45$.	
0 sec.	0.710	1.320	1.320	1.622	1.050	1.500	1.490	1.735
10	0.860	1.342	1.357	1.636	1.122	1.516	1.519	1.742
20	1.138	1.447	1.466	1.665	1.301	1.565	1.586	1.756
30	1.431	1.588	1.599	1.701	1.498	1.636	1.658	1.775
40	1.648	1.728	1.708	1.748	1.658	1.718	1.724	1.798
50	1.775	1.836	1.785	1.789	1.769	1.794	1.782	1.823
60	1.845	1.906	1.839	1.826	1.836	1.856	1.848	1.848
70	1.889	1.948	1.875	1.857	1.878	1.903	1.859	1.872
80	1.918	1.969	1.903	1.885	1.906	1.935	1.885	1.895
90	1.935	1.979	1.919	1.903	1.910	1.954	1.903	1.913
100	1.946	1.983	1.932	1.919	1.933	1.967	1.917	1.924

TABLE III

[The concentrations of A, B and AB have been expressed in m. moles per litre. The initial and maximum rates (I. R and M.R.) have been expressed in m. moles per litre per second].

Initial conc. (A).	Initial conc. (B).	Effective initial conc. (A).	Effective initial conc. (B).	I.R. × 10³.	$\frac{(A)(B)^2}{I.R.} \times 10^{-4}$.	M.R. × 10³.	(AB) at M.R.	$\frac{(AB)^2}{M.R.}$.
				$\mu = 0.12$.				
10	5	9.5	2.8	4.80	15.5	26.60	0.853	27.35
5	10	4.8	5.6	9.10	16.5	26.40	0.869	28.61
5	5	4.8	2.8	2.13	17.7	21.70	0.768	27.18
5	7.5	4.8	4.2	5.06	16.7	13.06	0.577	25.49
				$\mu = 0.25$.				
10	10	9.6	5.0	20.00	12.00	39.07	0.953	23.25
10	5	9.6	2.5	5.60	10.70	18.80	0.643	21.97
5	10	4.8	5.1	7.60	16.40	17.73	0.623	21.87
5	5	4.8	2.5	1.87	16.13	6.27	0.367	21.45
				$\mu = 0.45$.				
10	10	9.6	4.7	9.60	22.08	26.27	0.800	24.37
10	5	9.6	2.2	2.13	21.81	19.93	0.431	16.99
5	10	4.8	4.5	3.86	25.18	9.73	0.504	26.10
5	5	4.8	2.2	0.93	24.98	3.20	0.285	25.38

I.R. $= -d(AB)/dt$ (Initial). M.R. $= -d(AB)/dt$ (Maximum).

DISCUSSION

The nature of the log I—time curve of the coloured intermediate $FeS_2O_3^+$ clearly indicates that the rate of decay is not the maximum in the beginning but attains a maximum value after a period of time. With progress of the reaction, the ferrous and the tetrathionate ions replace respectively the ferric and the thiosulphate ions, and as a result there is a decrease in the ionic strength. That the gradual increase in the rate is not due to the change in ionic strength accompanying the reaction is demonstrated by the following considerations.

For a mixture containing initially equal volumes of solutions of strength $0.005M$ with respect to Fe^{3+} and $S_2O_3^{2-}$ ions, the change in ionic strength at the completion of the reaction would be 0.0175. Working with such a mixture at an ionic strength as high as 0.45, the autocatalytic nature of the curve could be observed and that, when the reaction is far from being complete. This shows that the change in ionic strength cannot be the reason for the increase in the rate of decay. Secondly, the instability constant

$$K_{FeS_2O_3^+} = \frac{(Fe^{3+})\ (S_2O_3^{2-})}{(FeS_2O_3^+)}\ .$$

It has been shown by Page (*Trans. Faraday Soc.*, 1954, **50**, 120) that the value of the instability constant decreases with decrease in ionic strength. So for the same concentrations of Fe^{3+} and $S_2O_3^{2-}$ ions, the concentration of $FeS_2O_3^+$ becomes more if the ionic strength be less. Let two successive stages of the reaction be imagined in which the concentrations of Fe^{3+} and $S_2O_3^{2-}$ are almost the same. That stage in which the ionic strength is less would have greater concentration of $FeS_2O_3^+$. It is evident therefore that with the progress of the reaction, which is accompanied by a decrease in ionic strength, the concentration of $FeS_2O_3^+$ at any moment should be more than that at the preceding instant, taking only the effect of the decrease in ionic strength into consideration. In other words, the change in ionic strength goes counter to the increase in the rate of decay observed in this reaction. Since $FeS_2O_3^+$ is an intermediate and its concentration is maximum when the concentrations of Fe^{3+} and $S_2O_3^{2-}$ are the maximum at the beginning, it is to be expected that the rate of consumption of $S_2O_3^{2-}$ or that of reduction of Fe^{3+} would be of the same nature as the rate of decay of $FeS_2O_3^+$. Experiments carried out (unpublished) confirm that the rate of consumption of $S_2O_3^{2-}$ is not the maximum at the beginning but attains maximum value after a period of time. All the above considerations lead us to accept that the decay of $FeS_2O_3^+$ must involve an intermediate for explaining the autocatalytic nature of the curve. This intermediate has been suggested by us to possess the formula $Fe(S_2O_3)_2^-$.

Without the assumption of the second intermediate, $Fe(S_2O_3)_2^-$, the manner in which the reaction can be imagined to occur is

$$2FeS_2O_3^+ = 2Fe^{2+} + S_4O_6^{2-}.$$

If this is so, it is evident that the rate in the beginning must be maximum, since the concentration of $FeS_2O_3^+$ is the maximum then. Further, as two ion-pairs of the same charge are involved, the rate of decay should increase with the increase in ionic strength, which is contrary to the observed data recorded in Table III. Moreover, the rate at the initial stage should vary as the square of the concentration of $FeS_2O_3^+$. In other words, $(Fe^{3+})^2\,(S_2O_3^{2-})^2$/initial rate should be constant. This is not so. On the other hand, $(Fe^{3+})\,(S_2O_3^{2-})^2$/initial rate is a constant, thereby showing that the initial rate does not vary with the square of $FeS_2O_3^+$ concentration.

From Table III both the initial and the maximum rates appear to decrease with the increase in ionic strength, suggesting that the rate-determining steps involve ions of opposite signs.

From the mechanism suggested, expressions for the initial and the maximum rates of decay have been derived. The data recorded in Table III are in good agreement with the expressions. The step represented by equation (*iii*) needs some explanation. In the presence of preponderating concentration of Fe^{3+}, it is worth while questioning the validity of this step. The inclusion of this step has been conceived on the tendency of the ferric ion to form the polynuclear compound $Fe_2(S_2O_3)_3$, however transient be its existence.

Here, though the mechanism of the ferric thiosulphate reaction has been discussed, the kinetic expression for the rates of decay of the coloured intermediate $FeS_2O_3^+$ has been derived and corroborated by experimental data. The expression for the rate of consumption of the thiosulphate or that of the reduction of the ferric ion will be published in due course. The mechanism proposed by us differs from the one proposed by Holluta and Martini (*Z. anorg. Chem.*, 1924, **141**, 23 ; 1925, **144**, 321) in that our mechanism includes two intermediates, $FeS_2O_3^+$ and $Fe(S_2O_3)_2^-$. Further, all stages of mechanism are simple bimolecular reactions, and it is thus in keeping with the general principle of economy of structural change in each elementary process.

DEPARTMENT OF CHEMISTRY,
RAVENSHAW COLLEGE,
CUTTACK-3

Received April 2, 1957.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

LIGHT SCATTERING IN SOAP-SOLVENT SYSTEMS. PART II. SODIUM STEARATE IN OCTYL AND IN DECYL ALCOHOL: INTENSITY MEASUREMENTS

By K. P. Buch

The measurement of the intensity of light scattered at different directions during the cooling of gel-forming systems of sodium stearate in octyl and in decyl alcohol has shown that the intensity of the light scattered increases while the value of the ratio I_{45}/I_{135} decreases during the cooling and gelation of these systems. These results indicate that the particles decrease in size and increase in number when these systems are cooled. It has been concluded from the values of the ratio I_{45}/I_{135} which lie between 2 and 3, that the particles in these systems are rod-shaped. The observed results have been explained on the considerations of the behaviour of soaps in polar solvents.

In a previous communication (Buch and Sundaram, *Proc. Nat. Inst. Sci., India*, 1954, **20**, 609) it has been observed from the measurement of the depolarisation factors of the light scattered from sodium stearate-octyl alcohol and sodium stearate-decyl alcohol systems that the particles, which are initially (at 130°) large and anisotropic, decrease in size and in anisotropy during the cooling and gelation of these systems. The present investigation deals with a study of the intensities of the light scattered from these systems at 45° (forward), 90° (transverse) and 135° (backward) to the direction of the incident light.

Experimental

The gel-forming systems were prepared in the same manner as described in Part I (Naik and Deshpande, this *Journal*, 1957, **34**, 555) as also the experimental arrangement for the measurement of intensity, excepting that the Nujol in the observation bath was initially kept at 130°.

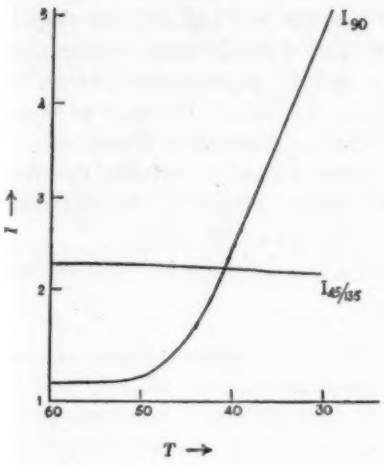
The results obtained showed that the variations in the intensity of light scattered at different temperatures were of the same nature for different concentrations of the soap. Fig. 1 shows the curves obtained by plotting the values of the intensity of transversely scattered light and the values of the dissymmetry ratio (I_{45}/I_{135}) against temperature, for the system containing 0.6% soap (temperature of gelation = 40°).

Discussion

It is seen from Fig. 1 that during the cooling of the system, the intensity of the light scattered remains constant until the temperature of the system is only a few degrees higher than the gelation temperature. On further cooling, the intensity inereases over

a short range and then again becomes constant. The increase in intensity of light scattered during the cooling of the system shows that the particles in these systems increase in number and/or size during the cooling and gelation of these systems.

FIG. 1



It is also seen from Fig. 1 that the value of the ratio $I_{45}/_{135}$ initially remains constant while cooling, then decreases for a time and again becomes constant below the gelation temperature. The decrease in the ratio I_{45}/I_{135} shows that size of the particles decreases during the cooling and gelation of these systems, thereby confirming the conclusions based on the variation of the values of ρ_h mentioned in the previous communication (Buch and Sundaram, *loc. cit.*). Hence, the increase in the values of the light scattered is due to the increase in the number of particles in the systems.

The observed decrease in size and decrease in anisotropy during the gelation of these systems bring out the difference between such systems and others containing a non-polar solvent. In the latter, ionic forces are absent whereas in the former, the presence of a polar solvent will cause its own effect. The solubility of the soap in the polar solvent like glycerine and glycol, even at a moderately high temperature, is low. On cooling from a high temperature, the system develops a mixture of a low proportion of spherical ionic micelles and a higher proportion of lamellar crystalline particles, similar to those formed by soap-water systems of high soap-concentration (McBain *et al.*, *J. Chem. Soc.*, 1922, **121**, 2325). The latter type of particles gives high value of ρ_v. The fall in solubility being very rapid in such systems, very little soap is left in the solution after the deposition of the first crop of mixture of particles. The deposition that takes place on subsequent cooling does not lead to any appreciable aggregation, as is shown by constancy of the I values. This may be due to the fact that the solutions have been depleted of soap and, hence, the particles deposited are tiny spheres incapable of agglomeration with previously deposited particles due to the peculiar orientation of soap-solvent molecules in them. During the cooling, the existing particles undergo thermal contraction, the spherical ones contracting equally in all directions. However, in the lamellar crystals, the thickness suffers negligible contraction as compared to their laminated surface. The concentration being in the longer dimension, the particles become less anisotropic in effect. Hence, the reduction in ρ_v values.

It is observed that an increase in the concentration of soap in the gel-forming systems containing octyl alcohol increases the intensity of the light scattered, but slightly decreases the final value of the ratio $I_{45}/_{135}$. Hence, it can be concluded that a system of a higher concentration contains a larger number of particles than one of a lower concentration.

According to Oster (Progress in Biophysics and Biophysical Chemistry", Butterworth-Springer Ltd., London, p. 80), the value of the ratio I_{45}/I_{135} increases rapidly with particle size in systems containing large independent particles and tends to a limiting value of 2.44 in the case of rod-shaped particles and 5.98 for disc-shaped particles. The size of the particles in the systems studied in the present investigation is quite appreciable as revealed by the low values of ρ_h and the unsymmetrical nature of the polarisation of scattering (cf. Buch and Sundaram, *loc. cit.*). Although in these systems the particles cannot be strictly considered as being independent of each other, still the fact that the values of the ratio $I_{45}/_{135}$ lie between 2 and 3 indicates that the particles are most probably rod-shaped. The fact that electron microscope investigation of soaps has shown them to be fibrillar in nature enhances such a possibility.

The author is grateful to Dr. Mata Prasad, D.Sc., F.N.I., F.R.I.C., and Dr. Sundaram for their interest in the progress of the work.

CHEMICAL LABORATORIES,
INSTITUTE OF SCIENCE,
BOMBAY 1.

Received January 12, 1957.

our. Indian Chem. Soc., Vol. 34, No. 9, 1957]

PREPARATION OF 2-ARYLAMINO-4-(2-THIENYL)-THIAZOLES AND THEIR AZO AND MERCURATED DERIVATIVES

By G. N. Mahapatra and M. K. Rout

Twelve new 2-arylamino-4-(2-thienyl)-thiazoles have been prepared by the condensation of different substituted thioureas with 2-thienylmethyl ketone and coupled with diazotised sulphanilamide. As expected, the sulphonamidophenylazo group enters the thiazole nucleus at position-5 in support of which some decisive evidences have also been stated. The thiazole compounds have been mercurated and the mercurated products tested for their bactericidal and fungicidal actions. Fungicidal results of the mercurated compounds are quite promising.

In view of the fact that antihistaminic properties are exhibited in a pronounced manner by both thiazolylamines and thiophene compounds (Saijo, *J. Pharm. Soc. Japan*, 1952, **72**, 1009 ; Dahlbom, *Acta Chem. Scand.*, 1950, **4**, 744 ; Fridman, *Zhur. Obshchei Khim.*, 1953, **23**, 278 ; Kyrides *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 745), an investigation on the preparation of some thiazole compounds containing a thiophene moiety was undertaken with the object of testing the compounds for the above properties as well as for other biological effects. Twelve compounds of this series have been prepared by condensing 2-thienylmethyl ketone with different N-substituted monoaryl thioureas in presence of iodine according to our method reported earlier (this *Journal*, 1953, **30**, 398). These thiazole derivatives have been characterised by their acetyl and picrate derivatives.

The recent interesting uses of azo dyes as powerful disinfectants (Ostromislensky, U. S. Pat. 1, 785, 327/1930) as insecticides in controlling European corn borer and for use on spider mite and Mexican beetle (Questel *et al.*, U.S. Dept. Agr. Bur. Entom. and PLT Quar., 1941, p. 557 ; Eddy and Carson, *J. Econ. Entom.*, 1946, **39**, 631) and as effective antiviral agents (Ueda *et al.*, *J. Pharm. Soc. Japan*, 1952, **72**, 1343), encouraged us to undertake the preparation of some azo derivatives of the above thiazole compounds. Since the azo derivatives derived from sulphanilamide produce the maximum of these effects, specially as antiviral agents (Hiyama, *ibid.*, 1952, **72**, 1374), these azo dyes have been prepared by coupling 2-aryl-substituted-amino-4-(2-thienyl)-thiazoles with diazotised sulphanilamide.

On the basis of earlier observations (Beyer and Wolter, *Chem. Ber.*, 1952, **85**, 1077 ; Erlenmeyer *et al.*, *Helv. Chim. Acta*, 1942, **25**, 1066 ; Ganapathi and Venkataraman, *Proc. Ind. Acad. Sci.*, 1945, **22A**, 348), it has been assumed that the azophenylsulphonamido group enters the thiazole nucleus and attaches to the C_5 position. The possibility of the azo group being linked to the aryl nucleus, attached to the amino group at C_2, is completely excluded by the fact that when the azo compound, prepared from diazotised sulphanilamide and 2-phenylamino-4 (2-thienyl)-thiazole, is reduced with sodium hydrosulphite, the resulting product containing a free amino group (m.p. 166° ; found : N, 14.93 ; S, 23.42 ; $C_{13}H_{11}N_3S_2$ requiring N, 15.38 ; S, 23.47%) is not identical with 2-(*p*)-aminophenylamino-4-(2-thienyl)-thiazole (m.p. 123° ; N, 15.11 ; S, 23.40 ;

$C_{13}H_{11}N_3S_2$ requiring N, 15.38 ; S, 23.47%) which is obtained from *p*-aminophenylthiourea and 2-thienylmethyl ketone by the usual procedure, reported earlier. The substitution of the hydrogen atom of the thiophene nucleus by the azo group is also ruled out on the following considerations.

It has been reported by Beyer and Wolter (*loc. cit.*) that when 4-phenyl-2-aminothiazole is coupled with benzenediazonium chloride, the azophenyl group does not attach to the phenyl nucleus at the carbon atom 4. It has also been reported by one of us (this *Journal*, 1956, **33**, 690) that when 2-amino-4-(2-thienyl)-thiazole is coupled with diazotised sulphanilamide, the azo group does not attach to the thiophene group at C_4, but to the C_5 of the thiazole nucleus. From this observation it may be concluded that the azo group does not go to the thiophene nucleus. Further support in favour of the azo group entering C_5 of the thiazole nucleus is afforded by the inability of 4 : 5-disubstituted-2-arylaminothiazoles of undergoing coupling with diazotised sulphanilamide, as reported earlier (this *Journal*, 1954, **31**, 933).

The thiazole compounds, prepared above, have also been mercurated with mercuric acetate with the formation of acetoxymercuri compounds to substantially augment the bactericidal as well as fungicidal activities of the thiazoles (cf. Das, Mahapatra and Rout, *ibid.*, 1955, **32**, 55 ; Rout *et al.*, *Nature*, 1954, **174**, 516). It has been assumed on the basis of the earlier work (Rout *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 4057 ; *J. Sci. Ind. Res.*, 1954, **13B**, 378) that the acetoxymercuri group enters the aryl nucleus attached to the amino group at C_2, at the *para*-position (with respect to - NH group) of the aryl nucleus and that if the *para*-position is blocked, the substitution occurs at the *ortho*-position. When the mercurated derivative of 4-(2-thienyl)-2-phenylaminothiazole is treated with bromine water or potassium perbromate solution, the acetoxymercuri group is knocked off, and is replaced by a bromine atom and the identity of this compound (m.p. 106° ; Br, 23.43 ; S, 18.45 ; $C_{13}H_9N_2BrS_2$ requiring Br 23.74 ; S, 18.98%) with 2-(*p*)-bromophenylamino-4-(2-thienyl)-thiazole (m.p. 107° ; Br, 23.31 ; S, 18.63 ; $C_{13}H_9N_2S_2Br$ requiring Br, 23.74, S, 18.98%) prepared from *p*-bromophenylthiourea and 2-thienylmethyl ketone lends decisive support in favour of the aryl nucleus undergoing mercuration. In case the aryl nucleus happens to be α- or β-naphthyl groups, the acetoxymercuri group enters the nucleus according to the rule of substitution in the naphthalene compounds.

The experimental procedures adopted for the preparation of thiazoles, their azo dyes and mercurated compounds have been illustrated with one example in each case in the Experimental.

EXPERIMENTAL

N-*Monoaryl-substituted Thioureas*.—The phenyl-, *o*-, *m*-, *p*-tolyl-, *o*-, *m*-, *p*-chlorophenyl-, *o*-, *m*-, *p*-carboxyphenyl-, α- and β-naphthyl-thioureas have been synthesised by the methods discussed earlier.

4-(2 - *Thienyl*) -2 - *phenylaminothiazole*.—A mixture containing phenylthiourea (6 g., 2 *M*), 2-thienylmethyl ketone (2.5 g., 1 *M*) and iodine (1 *M*) was heated under reflux for 12 hours on a water-bath and again for 12 hours after removal of the condenser. The deeply coloured crude reaction product was kept in contact with ether for 48 hours

with occasional shaking to remove the excess of iodine as well as the unchanged ketone. The ether was decanted off and the reaction product was kept in contact with a dilute solution of $Na_2S_2O_3$ for half an hour with occasional stirring. The resulting product was boiled with water to remove any unchanged thioureas. The residue was then treated with concentrated ammonium hydroxide, when a gummy product was obtained which did not solidify even on keeping in contact with ammonia for 4 days. The gummy product was made solid by converting it first to a solid picrate and subsequently decomposing the picrate with LiOH solution and extracting the desired compound with ether, yield 63%, m.p. 146°. (Found : N, 10.15 ; S, 24.13. Compound requires N, 10.95 ; S, 24.80%).

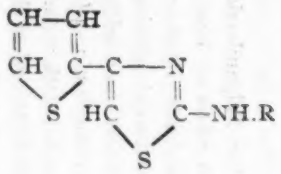
Thiazoles obtained from carboxyphenylthioureas were soluble in concentrated ammonia and were separated by acidifying carefully the ammoniacal solution with acetic acid. The thiazole bases were acetylated by heating them with acetic anhydride in presence of pyridine for about half an hour. The analytical data and properties of the thiazoles, their picrates and their acetyl derivatives are shown in Table I.

2-Phenylamino-4-(2-thienyl)-5-azophenyl-(p)-sulphonamidothiazole.—Sulpanilamide (0.8 g.) was dissolved in glacial acetic acid (2 c.c.) and diluted with water to 100 c.c. and diazotised with $NaNO_2$ (0.5 g. dissolved in 30 c.c. water) dropwise (until starch iodide showed an excess of HNO_2) in an ice-bath with efficient mechanical stirring. The resulting diazo solution being buffered with 10 g. of sodium acetate was added gradually with stirring to a previously well-cooled solution of 2-phenylamino-4-(2-thienyl)-thiazole (1 g. dissolved in 2 c. c. of acetic acid diluted to 40 c.c. with water), kept in an ice-bath. The reaction product was then stirred for another hour, when the orange-red azo dye separated out. This was collected by filtration and finally crystallised from alcohol, m.p. 181°, yield 71%. (Found : N, 15.96 ; S, 21.13. Compound requires N, 15.87 ; S, 21.77%). The properties and analytical data of the azo dyes are shown in Table II.

Mercuration of the Thiazoles.—To the thiazole compound (1 *M*), dissolved in alcohol-acetic acid solution, a solution of mercuric acetate (1.3 *M*) in water, acidified with dilute acetic acid, was added. Precipitate appeared in some cases after a while. The reaction mixture was kept overnight, filtered and washed thoroughly with hot water, dilute alcohol and finally with very dilute acetic acid. The properties and analytical data of the mercurated compounds are recorded in Table IV.

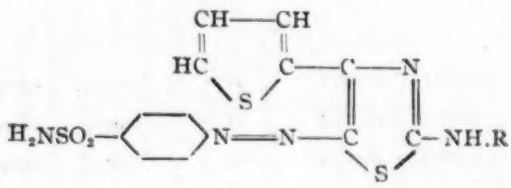
Bactericidal test.—The Rideal-Walker Serial Drop Dilution method was used for the comparative antibacterial activity. The bactericidal activity was measured in terms of maximum effective dilution (M.E.D.) of the thiazoles, their azo dyes and the mercurated thiazoles at 10 minutes' contact. The test organisms used were 24 hours' culture of *E. coli* and *Staph. aureus*. The mercurated compounds exhibited a very high activity, some of them being active in more than 1 : 80, 000 dilution. The bactericidal data of the compounds are recorded in Table III.

TABLE I



No. of compound.	Nature of the aryl group R	2-Arylamino-4-(2-thienyl)-thiazole. M.P.	Yield.	%Nitrogen. Found.	%Nitrogen. Calc.	%Sulphur. Found.	%Sulphur. Calc.	Picrate derivative. M.P.	Yield.	%Sulphur. Found.	%Sulphur. Calc.	Acetyl derivative. M.P.	Yield.	%Sulphur Found.	%Sulphur Calc.
1	Ph-	146°	63%	10.15	10.85	24.13	24.80	246°	79%	14.09	13.14	171°	90%	21.89	21.33
2	*o*-Tol.-	159°	71	10.82	10.29	23.89	23.53	117°	71	12.13	12.77	118°	89	20.87	20.38
3	*m*-Tol.-	131°	78	10.67	10.29	24.19	23.53	165°	65	12.81	12.77	141°	87	20.13	20.38
4	*p*-Tol.-	167°	67	10.43	10.29	24.31	23 53	127°	63	13.61	12.77	146°	81	19.89	20.38
5	(*o*)-Cl-C_6H_4-	109°	59	9.01	9.57	22.10	21.88	254°	59	11.89	12.27	98°	83	18.79	19.13
6	(*m*)-Cl-C_6H_4-	142°	63	8.78	9.57	21.31	21.88	157°	52	12.71	12.27	137°	78	20.11	19.13
7	(*p*)-Cl-C_6H_4-	211°	61	10.13	9.57	21.19	21.88	280°	57	12.59	12.27	181°	75	19.78	19.13
8	(*o*)-COOH-C_6H_4-	209°	65	9.11	9.27	20.89	21 19	155°	61	12.74	12.05	217°	71	19.51	18.60
9	(*m*)-COOH-C_6H_4-	205°	73	9.80	9.27	21.87	21.19	205°	62	11.91	12.05	219°	83	17.87	18.60
10	(*p*)-COOH-C_6H_4-	216°	71	9.71	9.27	21.10	21.19	261°	67	11.25	12.05	209°	76	18.13	18.60
11	α-$C_{10}H_7$-	122°	85	8.79	9.09	21.11	20.78	325°d	79	11.13	11.91	256°	93	18.81	18.28
12	β-$C_{10}H_7$	225° (decomp).	87	9.79	9.09	20.36	20.78	276°	78	12.51	11.91	245°d	91	18.70	18.28

TABLE II



2-Arylamino-4-(2-thienyl)-5-azophenyl-(p)-sulphonamidothiazole.

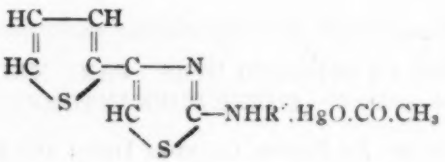
*No. of compound.	M. P.	Yield.	Colour of the azo dye.	%Sulphur.		%Nitrogen.	
				Found.	Calc.	Found.	Calc.
1	181°	71%	Orange-red	21.13	21.77	15.96	15.87
2	148°	67	Yellow	21.11	21.09	15.81	15.38
3	168°	63	Orange yellow	20.89	21.09	14.75	15.38
4	144°	69	Dirty-yellow	20.67	21.09	14.96	15.38
5	111°	59	Red	20.75	20.18	15.01	14.72
6	104°	65	Brownish-red	20.31	20.18	14.37	14.72
7	135°	71	Yellow	19.87	20.18	14.92	14.72
8	112°	53	Chocolate	18.99	19.79	14.79	14.43
9	261°	55	Chocolate	19.13	19.79	14.85	14.43
10	249°	59	Chocolate-red	19.63	19.79	13.79	14.43
11	158°	75	Chocolate	20.18	19.55	14.78	14.25
12	184°	85	Chocolate	20.34	19.55	14.61	14.25

* Nature of the aryl group R corresponds to those in Table I (column 2)

TABLE III

No. of comp. (vide Table I)	Bactericidal activity. M. B. D. E. Coli.	Staph. Aureus.	No. of comp. (vide Table II)	M. B. D. E. Coli.	Staph. Aureus.	No. of comp. (vide Table IV)	Fungicidal activity. M. B. D. E. Coli.	Staph. Aureus.	No. of comp. (vide Table IV)	No germination (In p p.m).	50% germination.
1	1 :2000	1 :4000	1	1 :1000	1 :2000	1	1 :40000	1 :40000	1	9	3
2	1 :2000	1 :4000	2	1 :1000	1 :2000	2	1 :20000	1 :40000	2	9	3
3	1 :2000	1 :4000	3	1 :1000	1 :2000	3	1 :20000	1 :40000	3	9	3
4	1 :2000	1 :4000	4	1 :1000	1 :2000	4	1 :20000	1 :40000	4	9	3
5	1 :2000	1 :4000	5	1 :1000	1 :4000	5	1 :40000	1 :80000	5	8	3
6	1 :2000	1 :4000	6	1 :1000	1 :4000	6	1 :40000	1 :80000	6	8	3
7	1 :2000	1 :4000	7	1 :1000	1 :2000	7	1 :40000	1 :80000	7	8	3
8	1 :1000	1 :1000	8	<1 :1000	1 :2000	8	1 :20000	1 :40000	8	12	5
9	1 :1000	1 :1000	9	<1 :1000	1 :2000	9	1 :20000	1 :40000	9	13	6
10	1 :1000	1 :1000	10	<1 :1000	1 :2000	10	1 :20000	1 :40000	10	13	6
11	1 :2000	1 :4000	11	1 :2000	1 :4000	11	1 :80000	1 :100000	11	8	3
12	1 :2000	1 :4000	12	1 :2000	1 :4000	12	1 :80000	1 :100000	12	8	3

TABLE IV



No. of the comp.	Nature of the group R'.	M. P.	Yield.	%Mercury. Found.	Calc.
1	-C_6H_4-	235°	71%	37.93	38.75
2	-(*o*)CH_3-C_6H_3-	192°	65	37.81	37.73
3	-(*m*)CH_3-C_6H_3-	226°	69	36.95	37.73
4	-(*p*)CH_3-C_6H_3-	291°	75	37.15	37.73
5	-(*o*)Cl-C_6H_3-	278°	73	35.78	36.33
6	-(*m*)Cl-C_6H_3-	204°	78	36.53	36.33
7	-(*p*)Cl-C_6H_3-	217°	76	36.81	36.33
8	-(*o*)COOH-C_6H_3	275°	61	35.13	35.71
9	-(*m*)COOH-C_6H_3-	>350°	63	35.51	35.71
10	-(*p*)COOH-C_6H_3-	>350°	59	35.83	35.71
11	-(α)-$C_{10}H_6$-	241°	86	34.91	35.33
12	-(β)-$C_{10}H_6$-	255°	89	35.83	35.33

Fungicidal Tests.—For fungicidal assay, the spore germination method of Montgomery and Moore (*J. Pomol & Hort. Sci.*, 1938, **15**, 553) with a slight modification has been used. *Piricularia orizae*, Cav. was used as the test fungus. The mercurated thiazoles are not very active as fungicides ; only 100 p.p.m. is active in inhibiting the spore germination. The mercurated compounds showed a high activity, being 100% effective in inhibiting the spore germination of the fungus at a concentration of 8 p.p.m., and at 3 p.p.m. the spore germination being 50% only. The data of the fungicidal test are recorded in Table III.

The authors wish to express their grateful thanks to Mr. Padmanavan, the Mycologist of the Central Rice Research Institute, Cuttack, for supplying the test fungus to carry out the fungicidal test, and to the Board of Scientific and Industrial Research, Orissa and to the Jnan Bijnan Parisad, Utkal University for grants assisting in carrying out these investigations.

MAYURBHANJ CHEMICAL LABORATORY,
RAVENSHAW COLLEGE,
UTKAL UNIVERSITY,
CUTTACK-3.

Received October 29, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

STUDIES IN INDIGOID DYES. PART XXI. 1:8-NAPHTHAPENTHIOPHENE-PHENANTHRENE-INDIGOS

By Paresh Chandra Dutta and Sunil Kumar Roy

The present communication deals with the study of thioindigoid dyes derived from phenanthrenequinone and 1 : 8-naphthoxypenthiophene with the object of comparing the colour of these dyes with isomeric dyes, described earlier.

A study of the colour and chemical constitution of thioindigoid dyes derived from phenanthrenequinone and thioindoxyl (this *Journal*, 1932, **9**, 99), phenanthrenequinone and benzthioindoxyls (*Ber.*, 1933, **66**, 1226 ; 1934, **67**, 5, 1319) has already been made and the conclusion arrived at has been embodied in Parts VI (*loc. cit.*), VIII (*Ber.*, 1935, **68**, 1447) and IX (*Ber.*, 1936, **69**, 2343). The present communication is a continuation of this work and deals with dyes derived from phenanthrenequinone and its derivatives and 1:8-naphthoxypenthiophene, and thereby completes the study of all the isomeric thioindigoid dyes derived from phenanthrenequinone and naphthoxythiophenes. From the earlier investigations it was concluded that the dyes derived from *o*-diketones and 5 : 6-benzthioindoxyl had the deepest colour, *i.e.*, the additional benzene ring, when fused into the 5- and 6- positions of thioindoxyl molecule so as to be equidistant from the indigo chromophore >C=O and the auxochrome S, was the most favourable position for producing deeper colour in these isomeric dyes. The dyes derived from 1 : 8-naphthoxypenthiophene and *o*-diketones also fulfill this condition of symmetry in the thioindoxyl part and, as such, these dyes are expected to be also deeper in colour. This expectation has been realised and the dyes are all very deep in colour and, in fact, they are the deepest coloured dyes in this series, even much deeper than the isomeric dyes derived from 5 : 6-benzthioindoxyl (2 : 3-naphthoxythiophene) as the comparison of absorption maxima given below will show. Of course, in 1 : 8-naphthoxypenthiophene, unlike other oxythiophenes, the -S-, =C=O and the reactive methylene group form part of a six-membered ring unlike five-membered one in the other cases studied, and so this six-membered ring, which is the distinguishing factor in this case, appears to have a much greater bathochromic effect than the usual five-membered thionaphthene ring.

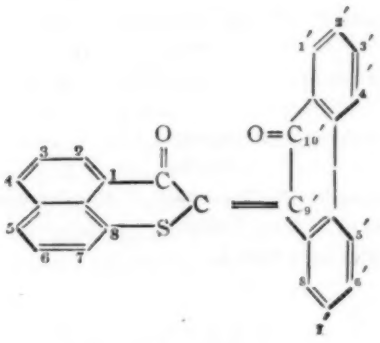
1 : 8-Naphthoxypenthiophene undergoes oxidation to *bis*-indigo very quickly, and so during condensation, the separate acetic acid solutions of the thioindoxyl and phenanthrenequinone and its derivatives were freed from dissolved air by passing CO_2, and during condensation also, the flow of CO_2 was continued. The dyes obtained are usually deep blue, and dissolve easily in nitrobenzene and pyridine with a blue solution. These are slightly soluble in acetic acid and insoluble in alcohol. Unlike the other isomeric dyes, these are very slightly soluble in alkaline hydrosulphite, and so full shades on cotton could not be obtained. In concentrated sulphuric acid these usually dissolve, producing a red or chocolate-brown colour. The absorption maxima of the two series in xylene solution are shown in Table I for the sake of comparison of colour.

TABLE I

[Nt, Npt, P and I denote respectively naphthathiophene, naphthapenthiophene, phenanthrene and indigo].

Name of the compound.	Absorption maxima.
2 : 3-Nt- 9′-P-I	575 mμ
1 : 8-Npt- „ „	590
2 : 3-Nt-9′-(2′-nitro)-P-I	580
1 : 8-Npt-„ „ „	625
2 :3-Nt-9′-(4′-nitro)-P-I	570
1 :8-Npt-„ „ „	625
2 :3-Nt-9′-(2′ : 7′-dinitro)-P-I	575
1 : 8 Npt-„ „ „ „	630

The structure of these compounds may be represented by the following general formula :



In mono-substituted phenanthrenequinones the condensation shown in the 9′-position is only provisional.

EXPERIMENTAL

1 : 8 - *Naphthapenthiophene - 9′ - phenanthrene-indigo.*—The separate solutions of phenanthrenequinone (1.04 g.) in hot acetic acid (25 c.c.) and 1 : 8-naphthoxypenthiophene (1 g.) in the same solvent (20 c.c.) were freed from dissolved air by passing CO_2 and then mixed together. The mixture, while the current of CO_2 had been continued, was treated with HCl (conc., 2 c.c.) and boiled for half an hour. The greenish brown solution became green and a dark precipitate gradually separated out. It was filtered while hot, washed with acetic acid and alcohol and crystallised from nitrobenzene as a dark chocolate crystalline mass, m.p. $> 300°$. It is easily soluble in nitrobenzene and pyridine, moderately soluble in hot xylene, slightly soluble in acetic acid and insoluble in alcohol. In alkaline hydrosulphite it is feebly soluble and so a very light violet shade could be obtained. In H_2SO_4 (conc.) it dissolves with a chocolate colour. Its absorption maxima in xylene solution is 590 mμ.

The method of preparation being similar except in the case of 2-aminophenanthrenequinone condensed product, where the condensation was carried out in alcoholic solution by anhydrous Na_2CO_3, the compounds with their properties are recorded below in a tabular form. They all have melting points above 300° and dissolve in H_2SO_4 (conc.), forming chocolate-brown or red colour. As the solubility in alkaline hydrosulphite is feeble in all cases, these cannot be regarded as good vat dyes.

TABLE II

1 : 8-*Naphthapenthiophene-phenanthrene-indigos.*

Name*	Prepared from 1 : 8-napthoxy-penthiophene and	Appearance	Crystallised from.	Absorption maxima.	Analysis Found.	Calc.
1 : 8-Npt-9′-P-I	P	Dark chocolate	Nitrobenzene	590 mμ	C ; 79.61	80.00
					H ; 3.72	3.59
1 : 8-Npt-9′-(2′-nitro)-P-I	2-nitro-P	Blue microscopic needles	Xylene	625	C ; 71.49	71.72
					H ; 3.05	2.98
1 : 8-Npt-9′-(4′-nitro)-P-I	4-nitro-P	Dark crystalline mass	,,	625	C ; 71.41	71.72
					H ; 3.11	2.98
1 : 8-Npt-9′-(2′-bromo) ,,	2-bromo-P	Do	,,	620	C ; 66.28	66 52
					H ; 2 89	2 77
1 : 8-Npt-9′-(2′-amino)- ,,	2-amino-P	Bluish violet needles	,,	620	C ; 76.72	77 03
					H ; 3 82	3.70
1 : 8-Npt-9′-(2′ : 7-dinitro)- ,,	2 : 7-dinitro-P	Blue crystalline mass	Nitrobenzene	630	N ; 5.67	5.83

The abbreviations are the same as in Table I.

CHEMICAL LABORATORY,
L. S. COLLEGE,
MUZAFFARPUR.

Received May 6, 1957.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

KINETICS OF THE REACTION BETWEEN FORMALDEHYDE AND AMMONIA

By Sameer Bose

The formation of hexamethylenetetramine has been studied in aqueous solutions at two different temperatures by mixing stoichiometric proportions of H.CHO and NH_4OH, and determining the rate of disappearance of the aldehyde. The reaction has been found to be a third-order one. The presence of an intermediate complex has been detected, which on hydrolysing with dilute acetic acid yields H.CHO and NH_4OH in equimolecular proportions. A three-step mechanism has been proposed involving a Mannich type of reaction.

Baur and Ruetchi (*Helv. Chim. Acta*, 1941, **24**, 754) studied the kinetics of this reaction by titrating ammonium hydroxide with the acid in presence of phenol red. They could not draw any definite conclusion, but indicated the probability of a third order reaction. It is felt that the reaction is a fast one, hence it becomes imperative that it should first be arrested and then the constituents estimated. Boyd and Winkler (*Canadian J. Res.*, 1947, **25B**, 387) studied this reaction from 0° to 35° and obtained three rate curves based on ammonia consumed, formaldehyde consumed and tetramine formed. The curves, specially at higher temperatures, were widely separated and so the order of the reaction could not be evaluated. In view of this uncertainty, a study of its kinetics was undertaken after having arrived at a new iodometric method of estimating formaldehyde in presence of ammonium salts and tetramine. The procedure is a modification of Romijn's hypoiodite method (*Z. anal. Chem.*, 1897, **36**, 19).

Experimental

Method of Evaluating Formaldehyde.—Romijn's method cannot be used in presence of ammonium salts as the reaction is carried out in the alkaline medium and the NH_4OH formed combines with I_2. It was observed that on adding a solution containing 3% $HgCl_2$ and about 40% KI, the interference caused by NH_4OH was completely prevented. The ammonium probably forms a soluble complex with K_2HgI_4 in presence of a large excess of KI. Synthetic mixtures of H.CHO (0.075*M*) and NH_4Cl (0.05*M*) were extensively analysed by this method, affording satisfactory results within 0.5% error (this *Journal*, 1957, **34**, 497). It has already been claimed by Dorrer and Ozimic (*Farm. Glasnik*, 1949, **5**, No. 9/10, 174) that tetramine does not interfere with Romijn's method.

The reaction mixture (5-10 c.c.) after freezing in 0.1 *N* acetic acid was pipetted out into a 100 c.c. conical flask and treated with a freshly prepared $HgCl_2$–KI solution (~8 c.c.). After adding 0.1 *N*-I_2 (10 c.c., by pipette) and 1.0*N*-NaOH (2 c.c.), the flask was corked and left for 20 minutes at about 20°. The contents were then acidified with 1.0*N*-HCl (4 c.c.), and the I_2 liberated was titrated with 0.05 *N* hypo solution to

starch end-point. A blank was carried out, similar in all respects except for the addition of the H.CHO mixture. The difference in the hypo readings gave the amount of I_2 consumed by H.CHO during its oxidation.

Arresting the Reaction.—The reaction being a comparatively fast one, care was taken in recording time precisely with a stop-watch. A mixture of NH_4OH and H.CHO stops reacting when acidified, but if a mineral acid is used, the tetramine formed hydrolyses to H.CHO and NH_4OH. A dilute solution of acetic acid was found more suitable as it had a negligible effect on tetramine The reaction was started in every case by adding the H.CHO solution from a fast pipette to a solution of NH_4OH and it was arrested by taking a definite volume of this mixture in a pipette and adding to an equal volume of 0.1 *N* acetic acid. The pipette used had a delivery time of 6 seconds. The acidified reaction mixture was allowed to stand for 20 minutes so as to decompose the intermediate complex and then an aliquot (5 to 10 c.c.) was pipetted out for evaluating H.CHO taking part in the formation of tetramine only.

The Order of the Reaction

(*a*). *By Half-life Method.*—An attempt was made to evaluate the order from the measurements of "half-life", by finding out the time required for the disappearance of half of the H.CHO, when mixed with a stoichiometric proportion of NH_4OH.

For a third order reaction, if the three reactants are in equal concentrations,

$$K_3 = \frac{1}{2t}\left\{\frac{1}{(a-x)^2} - \frac{1}{a_2}\right\}$$

if $\frac{1}{2}a$ is substituted for x,

$$t_{\frac{1}{2}} = \frac{3}{2k_3a^2}.$$

For two initial concentrations of A and a, if "half-lives" are $T_{\frac{1}{2}}$ and $t_{\frac{1}{2}}$ then

$$\frac{t_{\frac{1}{2}}}{T_{\frac{1}{2}}} = \frac{A^2}{a^2}.$$

The above expression has been applied to various initial concentrations of H.CHO and the "half-life" calculated. The results are recorded in Table I. The experimental and the calculated values are in fair agreement, showing that the contention of a third order reaction is correct.

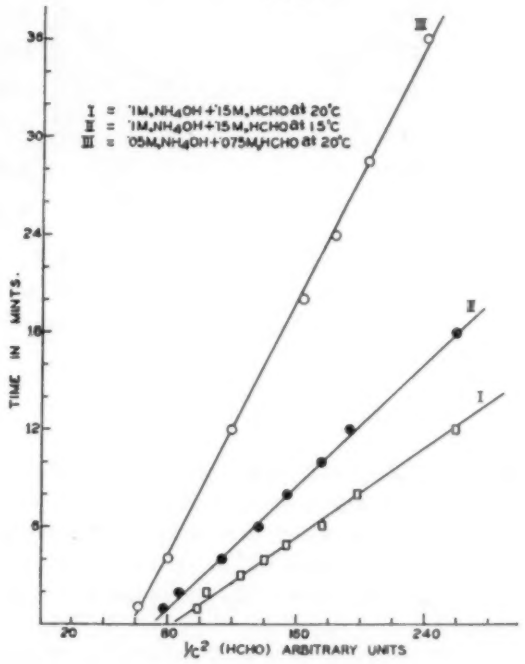
TABLE I

Initial conc.		Half-life at 20°.		Half-life at 15°.	
H.CHO.	NH_4OH.	Exp.	Calc.	Exp.	Calc.
0.15 *M*	0.10 *M*	6.0 min.	...	10.0 min.	...
0.10	0 067	13.5	13.5 min.	22.0	22.5 min.
0.075	0.05	23.0	24.0	38.5	40.0
0.06	0 04	36.5	37.5	61.0	62.5

(*b*). By *Plotting* $1/C^2$ *against Time.*—In a third order reaction $t \propto 1/C^2$, if the three reactants are in equal concentrations. In this case there are only two reactants, which, when present in stoichiometric proportions, yield a straight line (Fig. 1) on

plotting t against $1/C^2$, where C is the concentration of H.CHO. The reactions were followed to about 78% of completion.

FIG. 1



Intermediate Complex.—The reaction mixture containing H.CHO and NH_4OH, when acidified with dilute acetic acid, was found to contain an intermediate complex, which hydrolysed much more rapidly than tetramine. A study of the hydrolysis of 0.01 *M* tetramine solution by 0.05 *N* acetic acid at 20° revealed that it was a very slow process. It can be neglected when the two reactants come in contact for 20 to 30 minutes only. The intermediate complex, on the other hand, hydrolysed very rapidly and in 30 minute's time broke up completely into H.CHO and NH_4OH. Its hydrolysis was studied by mixing equal volumes of 0.15 *M*-HCHO and 0.1 *M*-NH_4OH and allowing the reaction to proceed to half completion and then it was arrested by pouring in an equal volume of ice-cold 0.1 *N* acetic acid. This acidified solution (10 c.c.) was immediately withdrawn for the estimation of H.CHO. The rest of the solution was kept at 20° and 10 c.c. pipetted out at various time intervals for evaluating H.CHO. The results, as recorded in Table II, show that the H.CHO content of the solution rapidly increases in the initial stages and attains a stable value after 30 minutes when the decomposition of the complex is complete.

TABLE II

Time.	Total H.CHO obtained (c.c. of 0.025 *M* soln.)	H.CHO obtained by hydrolysis of the complex (c.c. of 0.025 *M* soln.).
0 min.	6.15	...
5	7.30	1.15
10	7.80	1.65
15	8.00	1.85
30	8.25	2.10
45	8.20	2.05
60	8.25	2.10

The intermediate complex on hydrolysis also produced NH_4OH which, when estimated by titrating the acidified mixture with NaOH in presence of phenol red, was found to be in equimolecular proportion with H.CHO. Experiments were repeated several times to confirm this.

DISCUSSION

Polly *et al.* (*Canadian J. Res.*, 1947, **25B**, 525), who studied the action of ammonium salts on H.CHO from p_H 4 to 8, also postulated the formation of a byproduct because more NH_3 and H.CHO were consumed than could be accounted for by the formation of tetramine. Richmond *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 3659) put forward the view that $HN-CH_2-NH-CH_2-NH-CH_2$ (with the two terminal N atoms joined) was produced as an intermidiate complex. The present worker holds that there is an undeniable evidence in favour of the existence of an intermediate complex which is unstable in presence of dilute acetic acid and decomposes completely into equimolecular proportions of of H.CHO and NH_3. The complex which undergoes such a rapid hydrolysis is probably a simpler compound like $CH_2=NH$ or $CH.OH-NH_2$.

The probable mechanism of the reaction is :

(A) $H.CHO + NH_3 \rightleftharpoons H_2C=NH + H_2O$

[Complex A]

(B) $2\ H_2C=NH + CH_2O \dashrightarrow H_2C=N\text{-}CH_2-N=CH_2 + H_2O$

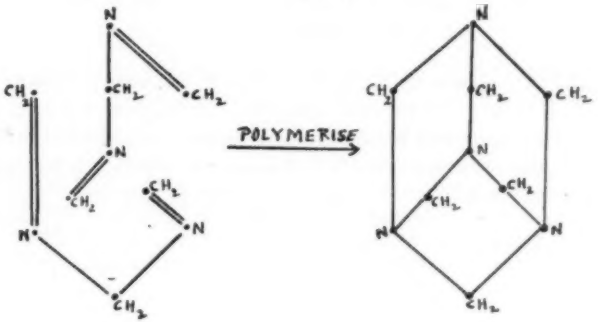
[Complex B]

(C) $2\ H_2C=N-CH_2-N=CH_2 \longrightarrow (CH_2)_6N_4$

No evidence can be adduced in support of the first step except for the detection of the intermediate complex. It is probably an instantaneous reaction which soon comes to an equilibrium. The second step is a Mannich type of reaction ; here the same molecule is the base and the active hydrogen compound. This reaction is a slow one and accounts for the disappearance of H.CHO in accordance with a third order reaction,

as already established. In the third step the complex B polymerises to furnish a more stable structure consisting of 3 interlocked hexagons, in the manner shown in Fig. 2.

FIG. 2



The author's thanks are due to Dr. V. Gore for facilities and to Dr. A. N. Kappanna for the incentive the author received for this work.

CHEMISTRY DEPAREMENT,
M. M. V., JABALPUR.

Received November 27, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

THE INFLUENCE OF AMINO-ACIDS ON THE AUTOXIDATION OF ASCORBIC ACID

By P. C. Rakshit, B. C. Sen and P. K. Bhattacharyya

The autoxidation of ascorbic acid in solution has been studied in presence of different amino-acids, like glycine, alanine, glutamic acid, aspartic acid, leucine etc., and amides like asparagine and guanidine. When these compounds are present in molecular proportions to ascorbic acid or in higher proportions, they exhibit a strong stabilising influence on the autoxidation. The amino-acids suffer no chemical change. The stabilising effect decreases with increase of temperature and p_H. It is suggested that this effect is probably due to a kind of loose association with ascorbic acid.

The most remarkable property of ascorbic acid is its reducing action which renders it liable to easy oxidation. This is obviously due to the two hydroxyl groups attached to the double bond in the closed lactone ring. In consequence, the substance avidly takes up oxygen in neutral and even in slightly acidic medium, to suffer the reversible conversion to dehydroascorbic acid.

Some of the early workers (Kellie and Zilva, *Biochem. J.*, 1935, **29**, 1028; Baron *et al.*, *J. Biol. Chem.*, 1936, **112**, 625), mostly using natural ascorbic acid, suggested that pure ascorbic acid did not undergo autoxidation. The spontaneous aerobic change is due to the presence of traces of positive catalysts, specially copper ions. Ghosh *et al.* (*Biochem. Z.*, 1936, **289**, 15; *Z. physikal. Chem.*, 1937, **115**, 246) showed that solutions of synthetic ascorbic acid suffered reversible autoxidation between p_H 6.8 and 7.2, with no trace of iron or copper.

This autoxidation acquires a special importance when the influence of other substances, specially those with which it is associated in nature, is studied. To illustrate, Caro and Giani (*Z. physiol. Chem.*, 1934, **223**, 13) observed that sugars had no influence on its autoxidation. Traces of sulphydril compounds completely suspended the oxygen uptake by ascorbic acid solution at about p_H 7.0 (Ghosh *et al.*, *Biochem. Z.*, 1936, **289**, 15; 1937, **294**, 330). Chlorophyll also exerts inhibitory action on the process (Giroud, *Compt. rend. Soc. Biol.*, 1934, **117**, 612; Rakshit, *Biochem. Z.*, 1938, **297**, 153; Bessey, *J. Biol. Chem.*, 1933, **103**, 687).

Occasional observations are also recorded on the effect of amino-acids on the autoxidation of ascorbic acid. In growing tissues of plants, protein-ascorbic acid complex is supposed to exist and be decomposed at higher temperature (Reidman *et al.*, *Biochem. J.*, 1938, **32**, 85). Caro *et al.* reported that glycine and alanine exhibited some retarding influence on the autoxidation of ascorbic acid (*Chem. Abs.*, 1944, 6383 : 1943, 6719; *J. Osaka Med. Soc.*, 1940, **39**, 473). But Peterson and Walton (*J. Amer. Chem. Soc.*, 1943, **65**, 1212) found glutamic acid, aspartic acid and cystiene not to retard aerobic decomposition of ascorbic acid. Krishnamurthi and Giri (this *Journal*, 1941, **18**, 191) found that amongst others, glycine and alanine partially prevented autoxidation of

ascorbic acid, when catalysed by copper. It is reported that valine, leucine, histidine, arginine etc. cannot protect the oxidation of ascorbic acid (*Kyoto Univ. Bull. Res. Inst. Food. Sci.*, 1949, **1**, 35). It was therefore considered necessary to make a detailed study of the influence of amino-acids on the aerobic oxidation of ascorbic acid.

EXPERIMENTAL

Synthetic ascorbic acid of Hofman-la-Roche was used throughout. Its purity was checked up by titration against I_2 (solution) and optical rotation. Amino-acids and other chemicals used were of reagent quality. All solutions were made from bidistilled water from all-pyrex stills. Special precautions were taken to avoid contamination of the catalysts. The absence of copper and iron ions was always confirmed by rubeanic acid, sulphocyanides etc.

The oxidation was studied by bubbling pure air at a considerably rapid rate (approx. 70–80 bubbles per min.) through a definite volume of the solution. In each of these experiments, a blank control was also linked to the system without the amino-acid, so that any variation in the external factors could be counteracted. The p_H was rigorously kept constant in each of the reaction and control vessels. Normally phosphate buffers were used; acetate and borate buffers were employed only in special cases.

The apparatus for studying the oxidation was a simple one. Two wide-mouthed pyrex tubes fitted with rubber corks, carrying delivery tubes, were used as oxidation vessels and the control. Equal volumes of the solution of the reaction mixture and its blank were taken in them and subjected to the same continuous flow of washed and purified air through them in fine bubbles. The temperature of the reaction vessels was kept constant correct to $\pm 1°$.

From time to time an aliquot part of the reaction mixture as also the blank was pipetted off into dilute H_2SO_4 and quickly titrated against the standard iodine solution ($\sim N/100$).

The first set of experiments were to establish that the solution of ascorbic acid, even when free from detectable traces of Cu and Fe ions, suffered oxidation in air at p_H 7.0 and at different temperatures. The results are recorded in Table I.

TABLE I

$p_H = 6.8$

Conc. of ascorbic acid.	Temp.	I_2 conc. ($N/100$)	Iodine titre for 1 c.c. soln. after 180 min.	% Ascorbic acid oxidised.
0.02 $\frac{m}{M}$	35°	1.0024	1.85 c.c.	61.0
0.0238	25°	1.082	1.95	56.7
0.0229	0°	1.010	3.40	25.3

The oxidation was then studied in presence of several amino compounds: glycine, alanine, glutamic acid, aspartic acid, leucine, guanidine and asparagine. The influ-

ence of each ot them was also studied with variation of p_H, temperature, etc. As a general rule, these substances protect ascorbic acid against aerobic oxidation. The results are shown in Tables II and III.

TABLE II

Conc. of ascorbic acid.	Reaction mixture Asc. acid : amino-acid.	p_H.	Temp.	I_2 titre of ascorbic acid at 0 min.	I_2 titre of ascorbic acid at 180 min.	% Ascorbic acid oxidised. Blank.	% Ascorbic acid oxidised. Reaction vessel.
			Glycine.				
0.0998	2 : 1	6.9	24°	6.35	4.95	28.0	22.0
0.105	1 : 1	6.9	,,	6.35	5.75	30.4	9.5
0.101	1 : 4	6.9	,,	6.25	6.06	28.0	4.0
0.0515	1 : 2	6.7	,,	4.75	4.30	23.7	9.5
0.05	1 : 2	7.1	,,	4.50	4.00	41.0	11.0
0.0501	1 : 2	7.8	25°	4.50	3.10	51.7	31.0
0.103	1 : 2	6.8	30°	6.40	5.20	37.0	18.7
			Alanine.				
0.053	1 : 1	6.9	25°	8.50	5.80	49.4	31.8
,,	1 : 2	,,	,,	3.25	2.30	55.4	29.0
,,	1 : 2.5	,,	,,	8.70	6.60	57.8	24.0
,,	1 : 4	6.8	,,	8.80	6.95	43.5	21.0

Estimation of the Amino-acids:—After definite intervals of time, not only the ascorbic acid was estimated, but also the amino-acids, in order to ascertain if the latter would participate the chemical process. Glycine and alanine were estimated by alkali titration by fixing the NH_2 group with formaldehyde. Glutamic acid was estimated by Pope and Stevens' method (*Biochem. J.*, 1939, **33**, 1069) by forming copper-complex. Asparagine was estimated colorimetrically by matching the intense blue colour of its copper-complex with standards prepared with known quantities. The amounts of guanidine were determined gravimetrically (Sharp, *ibid.*, 1920, **14**, 46) as picrates.

Influence of Glycine and Alanine on the Autoxidation of Ascorbic Acid.—In Table III are incorporated the results of the influence of glycine and alanine on the oxidation of ascorbic acid by air under different conditions of temperature, p_H etc.

Obviously, the two amino-acids stabilise the vitamin against aerobic oxidation. In most of these experiments the amino-acid was estimated, and not the slightest change in its concentration was observed. The stabilising effect increased with increased amino-acid concentration.

The Influence of other Amino Compounds.—Leucine, aspartic acid, glutamic acid as well as guanidine and asparagine also exert inhibitory action on the autoxidation of the ascorbic acid. The summarised results are only recorded in Table III.

It is evident from the results shown above, that not only the amino-acids but also some amides like guanidine and asparagine protect ascorbic acid from autoxidation, and the rate of oxidation is found to decrease with increasing concentration of ascorbic

acid. When the amino-acids are present in quantities less than one-fourth of that of ascorbic acid in molar proportions, there is no stabilising effect. The amides tried here have a greater effect.

TABLE III

Reaction mix. Asc acid : glutamic acid.	p_H.	Temp.	% Ascorbic acid oxidised in 180 mins. Blank vessel.	Reaction vessel.
1:4	6.8	25°	56.7	11.4
1:2	,,	,,	56.7	13.7
1:1	,,	,,	56.7	37.5
2:1	,,	,,	59.0	44.3
1:2	7.8	,,	42.8	12.9
1:2	6.2	,,	61.8	26.6
1:2	6.8	0°	25.3	4.5
1:2	,,	35°	61.1	150
Asc. acid : aspartic acid.				
1:4	,,	25°	64.9	15.2
1:2	,,	,,	64.4	16.6
1:7	,,	,,	64.2	23.1
2:1	,,	,,	62.0	31.1
1:2	,,	0°	30.1	8.3
1:2	,,	35°	71.0	30.6
Asc. acid: leucine.				
1:2	,,	25°	66.0	4.2
2:3	,,	,,	71.4	9.6
2:1	,,	,,	71.4	11.7
Asc. acid: luceine.				
1:2	7.6	25°	61	8.2
1:2	6.8	35°	75.4	9.2
Asc. acid: asparagine.				
1:2	6.8	25°	69	13.4
3:2	,,	,,	69	16.6
5:1	,,	,,	63	42.7
10:1	,,	,,	63	54.7
1:2	7.8	,,	61	23.6
Asc. acid: guanidine				
1:2	6.8	25°	69	6.3
1:1	,,	,,	66.3	17.9
1:2 (approx)	6.0	30°	54	8.0

The idea that amino-acids remove the positive catalysts (such as copper) and thereby exercise a protecting action may be rejected on the ground that this effect is observed only when the proportion of amino-acid to ascorbic acid is equal, or even greater. The possibility of amino acid inhibiting the reaction by using up some of the oxygen is also discarded by the fact that the contents of amino compounds remain unchanged after the reaction. We can only suggest that since molecular proportions of amino acids seem to be essential for inhibition of the autoxidation, there may be the formation of a loose molecular compound between the ascorbic acid and the amino-acid, rendering

the vulnerable OH groups inactive in the oxidation process. It must be remembered that amino-acid can prevent aerobic oxidation but not the iodometric oxidation of the ascorbic acid molecule.

The presence of ammonium salts, sugars, acetamide, urea and other simple amines has no effect on the spontaneous aerobic oxidation of ascorbic acid. β-Amino-acids, or aminobenzoic acids cannot also inhibit the process. It is therefore likely that there is a loose association, which prevents the formation of the intermediate tetrahydroxy compounds known to be first formed during autoxidation.

PRESIDENCY COLLEGE,
CALCUTTA.

Received August 3, 1956.

CITRATE COMPLEX OF CADMIUM

BY RABINDRA K. PATTANAYAK AND S. PANI

The citrate complexes of cadmium have been studied by p_H titration method. Three complexes, one neutral (C) and two anionic (C_1^- and C_2^{2-}) containing one citrate ligand per atom of cadmium, have been found to be formed. The equilibrium constant of the reactions $Cd^{2+} + H_3Cit \rightleftharpoons C + 2H^+$ (I) $C \rightleftharpoons C_1^- + H^+$ (II) and $C_1^- \rightleftharpoons C_2^{2-} + H^+$ (III) are respectively 6.43×10^{-7}, 1.59×10^{-5} and 4.86×10^{-9}. The hydroxyl group of the citrate ligand reacts but the proton is not liberated. The probable structures of the complexes C, C_1^- and C_2^{2-} have been discussed.

Citrate and tartrate are very interesting ligands. The utilisation of the alcoholic group in the formation of complex with trivalent antimony has been reported (Das and Pani, this *Journal*, 1955, **32**, 537; Samantara and Pani, *ibid.*, 1955, **32**, 165). A proton is usually liberated from the hydroxyl group due to such reactions. Cadmium has been reported to have a less tendency to form complex with oxygen than is observed with zinc (Sidgwick, "The Chemical Elements and their Compounds", Clarendon Press, 1950, p. 275). It would therefore be of interest to study the citrate complex of cadmium.

Polarographic study of cadmium citrate complex has been done by Meites (*J. Amer. Chem. Soc.*, 1951, **73**, 3727). The reaction $Cd^{2+} + C_6H_8O_7 \rightleftharpoons CdC_6H_6O_7 + 2H^+$ has been investigated by potentiometric method and the equilibrium constant has been reported to be 5.70×10^{-4} at 25° (Shin Shuzuki, *Sci. Rpts. Res. Inst. Tohoku Univ.*, 1953, **5A**, 16). All these investigations do not provide a clear picture of the system at different p_H, and no attempt has been made for a structural representation of the complex. The investigation of citrate complex of cadmium done by p_H titration is described below.

EXPERIMENTAL

The chemicals used were of Analar quality. p_H of the solution was measured by a Marconi p_H-meter.

Experiment (I).—The solution (105 c.c.) containing cadmium sulphate (0.0025 g. mol.), citric acid (0.003 g. mol.) and KNO_3 (0.025 g. mol.) and another solution (105 c.c.) containing KNO_3 (0.025 g. mol.) and citric acid (0.003 g. mol.) were titrated against 0.5*N*-NaOH solution. KNO_3 was added to maintain very nearly the same ionic strength in both the solutions. The results are graphically shown respectively by the curves (B) and (A) in Fig. 1. The temperature was 33°±0.5°. A white precipitate of cadmium hydroxide was obtained in the system containing cadmium salt above p_H 4.8 and a portion of the precipitate dissolved near about p_H 7.0 No such precipitate was obtained in another experiment containing a large excess of citric acid compared to cadmium (Fig. 2: curve A represents the p_H titration of 175 c.c. of

solution containing 0.0125 g. mol. of citric acid and B that of the same volume of solution containing the same amount of citric acid and 0.00125 g. mol. of cadmium sulphate against *N*-NaOH). It is evident from Figs. 1 and 2 that acid is liberated due to the reaction of cadmium with citrate ligand even at lower p_H. The horizontal distance, which is a measure of the amount of the acid liberated, increases at first with increasing p_H and then decreases. Above p_H 6.5, the horizontal distance is negligible.

DISCUSSION

Let A and B be two points on the same p_H axis intersecting the curves (A) and (B) respectively. The reaction taking place in the solution containing no cadmium is neutralisation of citric acid whereas in the other solution the complex is formed besides the neutralisation of citric acid. Let $[H_3Cit]_A$, $[H_2Cit^-]_A$, $[HCit^{2-}]_A$ and $[Cit^{3-}]_A$ be respectively the molar concentration of citric acid, dihydrogen citrate ion, monohydrogen citrate ion and citrate ion at A. Let $[Ct]_A$ and $[NaOH]_A$ be respectively the molar concentration of total citrate and sodium hydroxide added at A. The concentrations at B are similarly expressed. The concentration of hydrogen ion being the same at A and B is represented by $[H^+]$. Let k_1, k_2 and k_3 be respectively the first, the second and the third dissociation constant of citric acid ($k_1 = 8.32 \times 10^{-4}$, $k^2 = 4.07 \times 10^{-5}$ and $k_3 = 3.24 \times 10^{-6}$; Schwarzenbach and Ackermann, *Helv. Chim. Acta*, 1949, **32**, 1682).

$$\text{At A,} \quad [NaOH]_A + [H^+] = [H_2Cit^-]_A + 2[HCit^{2-}]_A + 3[Cit^{3-}]_A$$

$$= [H_3Cit]_A \times \left(\frac{k_1}{[H^+]} + 2\frac{k_1.k_2}{[H^+]^2} + 3\frac{k_1.k_2.k_3}{[H^+]^3}\right)$$

$$\text{or} \quad [NaOH]_A + [H^+] = a\,[H_3Cit]_A \quad \ldots \quad \ldots \quad (1)$$

$$\text{where} \quad a = \frac{k_1}{[H^+]} + 2\frac{k_1.k_2}{[H^+]^2} + 3\frac{k_1.k_2.k_3}{[H^+]^3}$$

$$[Ct]_A = [H_3Cit]_A + [H_2Cit^-]_A + [HCit^{2-}]_A + [Cit^{3-}]_A$$

$$= [H_3Cit]_A \times \left(1 + \frac{k_2}{[H^+]} + \frac{k_1.k_2}{[H^+]^2} + \frac{k_1.k_2.k_3}{[H^+]^3}\right)$$

$$\text{or} \quad [Ct]_A = b \times [H_3Cit]_A \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

At B the formation of the complex which takes place besides the neutralisation of citric acid may be represented by

$$Cd^{2+} + H_3Cit \rightleftharpoons C + n\,H^+ \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

C is the complex and the charge, if any, is not shown. The equilibrium constant is given by equation (3-1) where [C] and $[Cd^{2+}]$ are respectively the molar concentrations of the complex and the cadmium ion at B.

$$\frac{[C] \times [H^+]^n}{[Cd^{2+}] \times [H_3Cit]_B} = K \quad \ldots \quad \ldots \quad (3\text{-}1)$$

At B, $[NaOH]_B + [H^+] = n\,[C] + [H_2Cit^-]_B + 2[HCit^{2-}]_B + 3[Cit^{3-}]_B$

or $[NaOH]_B + [H^+] = n[C] + a \times [H_3Cit]_B$ ... ... (4)

Subtracting equation (1) from (4) one gets

$[NaOH]_B - [NaOH]_A = n[C] + a\,([H_3Cit]_B - [H_3Cit]_A)$

or $\Delta[NaOH] = n[C] + a\,\Delta[H_3Cit]$ ... ... (5)

Again, $[Ct]_B = [C] + H_3Cit]_B + [H_2cit^-]_B + [HCit^{2-}]_B + [Cit^{3-}]_B$

or $[Ct]_B = [C] + b\,[H_3Cit]_B$ ... ... (6)

Subtracting equation (2) from (6) one gets

$[Ct]_B - [Ct]_A = [C] + b\,([H_3Cit]_B - [H_3Cit]_A)$

or $\Delta[Ct] = [C] + b\,\Delta[H_3Cit]$

or $\Delta[H_3Cit] = \frac{1}{b}\,(\Delta[Ct] - [C])$ ... ... (7)

Substituting the value of $\Delta[H_3Cit]$ from equat on (7), the equation (5) reduces to

$$\frac{\Delta[NaOH] - \frac{a}{b}\,\Delta[Ct]}{[C]} = n - \frac{a}{b} \quad \ldots \quad \ldots \quad (8)$$

When the formation of the complex is complete, the concentration of the complex is equal to the concentration of cadmium sulphate $[CdSO_4]$. Hence

$$\frac{\Delta[NaOH] - \frac{a}{b}\,\Delta[Ct]}{[CdSO_4]} = n - \frac{a}{b} \quad \ldots \quad \ldots \quad (9)$$

$[H^+]$, $[Ct]_A$, $[Ct]_B$, $[NaOH]_A$ and $[NaOH]_B$ are calculated from the curves in Fig. 1. $\Delta[NaOH]$, $\Delta[Ct]$, $[CdSO_4]$ and a/b are calculated at different p_H.

Substituting these in equation (9), the value of n is obtained. The value of n is very nearly 2 at p_H 4.2 and less than 2 towards the lower p_H range and more than 2 towards the higher p_H range.

Assuming n to be two below p_H 4 2, $[C]$ is calculated by equation (8). $[Cd^{2+}]$ is obtained by subtracting $[C]$ from $[CdSO_4]$. The equilibrium constant of the reaction (3) is calculated by equation (3-1). The values are shown in Table I. The mean value of the equilibrium constant is 6.43×10^{-7}.

TABLE I

p_H.	a/b.	$\Delta[NaOH] \times 10^3$.	$-\Delta[Ct] \times 10^3$.	$[CdSO_4] \times 10^3$.	$[C] \times 10^3$.	$[Cd^{2+}] \times 10^3$.	$[H_3Cit]_B \times 10^3$.	$K \times 10^7$.
2.8	0.3585	2.27	1.300	2.315	1.191	2.196	1.726	11.00
3.0	0.4822	3.10	1.700	2.290	1.750	2.115	1.379	7.55
3.2	0.6738	3.91	2.400	2.267	2.503	2.017	1.082	5.27
3.4	0.7034	5.61	3.100	2.241	3.653	1.876	0.660	4.47
3.6	0.9069	6.87	4.300	2.212	5.211	1.691	0.4396	3.68
3.8	1.150	9.83	5.700	2.185	9.114	1.274	0.2245	5.10
4.0	1.203	12.02	6.900	2.155	11.680	0.987	0.1108	6.74
4.1	1.282	11.93	6.700	2.146	12.570	0.889	0.07731	6.80

For the p_H range above 4.2, n is calculated at different p_H values by equation (9), substituting the corresponding values of $\Delta[NaOH]$, $\Delta[Ct]$, a/b and $[CdSO_4]$. The values, thus obtained, are recorded in Table II

n being greater than 2, the formation of the complex C is complete and the increase in proton to cadmium ratio is due to the reaction,

$$C \rightleftharpoons C_1^- + H^+ \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

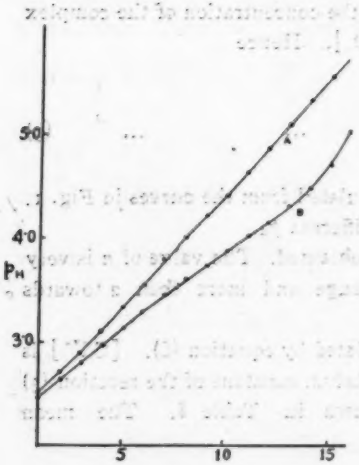
the equilibrium constant of which is given by

$$\frac{[C_1^-] \times [H^+]}{[C]} = K_1 \quad \ldots \quad \ldots \quad \ldots \quad (10\text{-}1)$$

where $[C_1^-]$ is the molar concentration of the complex C_1^-. The whole of the cadmium in the solution would be present partly as C and partly as C_1^-. Hence,

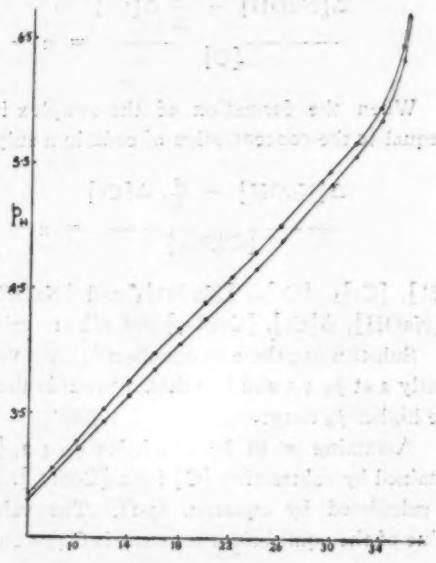
$$[C] + [C_1^-] = [CdSO_4] \quad \ldots \quad \ldots \quad (11)$$

FIG. 1



NaOH *in c.c.*

FIG. 2



NaOH *in c.c.*

Due to the formation of C and C_1^- from cadmium ion and citric acid, respectively, two and three protons are liberated. The total proton liberated due to the formation of the complexes is equal to $2[C] + 3[C_1^-]$. Hence,

$$\frac{2[C] + 3[C_1^-]}{[CdSO_4]} = n$$

or

$$\frac{2([C] + [C_1^-])}{[CdSO_4]} + \frac{[C_1^-]}{[CdSO_4]} = n$$

or $$\frac{[C_1^-]}{[CdSO_4]} = n - 2 \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

Hence, $$\frac{[C]}{[CdSO_4]} = 3 - n \quad \ldots \quad \ldots \quad \ldots \quad (13)$$

The equilibrium constant K_1 of the reaction (10) can be calculated by substituting $[C_1^-]/[CdSO_4]$ and $[C]/[CdSO_4]$ instead of the exact values of $[C_1^-]$ and $[C]$ respectively in equation (10-1). The values of K_1, thus calculated, are shown in Table II, the mean value being 1.59×10^{-5}.

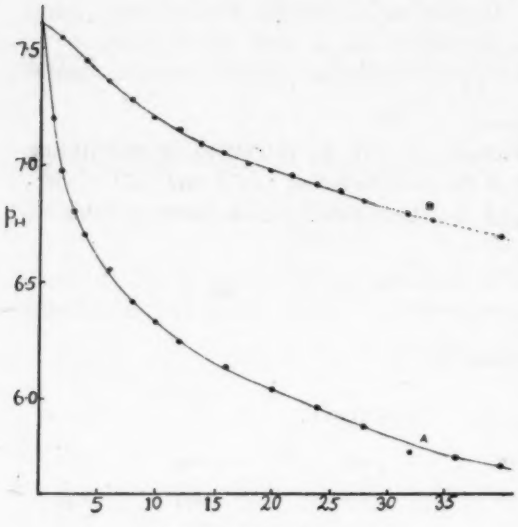
TABLE II

p_H.	a/b.	$\Delta[NaOH] \times 10^2$.	$-\Delta[Ct] \times 10^4$.	$[CdSO_4] \times 10^2$.	n.	$K_1 \times 10^5$.
4.35	1.487	1.358	7.70	2.116	2.1831	1.00
4.40	1.531	1.429	8.20	2.110	2.2674	1.45
4.45	1.573	1.421	8.20	2.104	2.3097	1.59
4.50	1.614	1.416	8.30	2.101	2.3517	1.72
4.55	1.659	1.409	8.00	2.095	2.3950	1.84
4.60	1.703	1.402	8.00	2.092	2.4383	1.96

The precipitate obtained above p_H 4.8 is cadmium hydroxide (it is free from citrate). The formation of cadmium hydroxide results from the competition of hydroxyl ion and citrate ligand for the small amount of cadmium ion in solution. The free citrate ligand in the system is small and very nearly constant. The increase of p_H introduces increasing amount hydroxyl ion in the solution and, hence, at $p_H > 4.8$, the solubility product of $Cd(OH)_2$ is exceeded. In presence of a large excess of citrate ligand $Cd(OH)_2$ is not precipitated as the concentration of cadmium ion is small and the solubility product of $Cd(OH)_2$ is not reached. It is, however, strange to note that in presence of excess of citrate, the precipitate of $Cd(OH)_2$ is not obtained even by increasing the concentration of OH^- ion hundred to thousand times (at p_H 6.8 or 7.8). Another reaction probably takes place at a higher p_H. To investigate the system at higher p_H the following method was adopted.

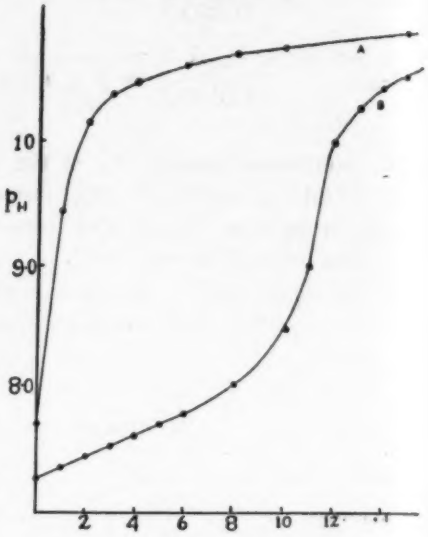
Experiment (II).—A solution (75 c.c.) containing KNO_3 (0.025 g. mol.) and sodium citrate (0.005 g. mol.) was titrated against 0.05*M*-HCl in one experiment and 0.05*M* cadmium sulphate solution in another experiment. The results are shown in curve (A) and (B) respectively in Fig. 3. (The experimental temperature was $30° \pm 0.5°$). The p_H's of both the systems are lowered, but the rate of decrease in the system to which hydrochloric acid is added is greater. Broken line in the curve indicates precipitation.

FIG. 3



$CdSO_4$ (*or* HCl) *in c.c.*

FIG. 4



NaOH *in c.c.*

The reactions taking place in the system to which hydrochloric acid is added is the neutralisation of the acid by the basic citrate ion, and formation of $HCit^{2-}$, H_2Cit^- and H_3Cit. In the other system to which cadmium sulphate is added, a proton is liberated due to the reaction of cadmium ion with citrate ion. A doubly charged anionic complex C_2^{2-} is formed before the precipitate separates out from the solution.

$$Cd^{2+} + Cit^{3-} \rightleftharpoons C_2^{2-} + H^+ \quad \ldots \quad \ldots \quad (14)$$

Since at the beginning the citrate ion present in the solution is in large excess compared to the amount of cadmium added, the condition for complete formation of the complex exists and the proton equivalent to the amount of cadmium sulphate added is expected to be liberated if no other reaction takes place, and the p_H of the two systems, at least in the beginning, is expected to be the same for the same amount (molar) of hydrochloric acid and cadmium sulphate added. This is, however, not observed. The deviation is not due to incomplete formation of the complex, as there is evidence of complete formation of C and C_1^- at lower p_H even in presence of a small excess of citrate. It is therefore very probable that the complex C_2^{2-} is more basic than citrate ion and a major portion of the proton liberated by reaction (14) is removed by reaction (15), and very little of $HCit^{2-}$, H_2Cit^- and H_3Cit is formed.

$$C_1^- \rightleftharpoons C_2^{2-} + H^+ \quad \ldots \quad \ldots \quad \ldots \quad (15)$$

The complex C_1^- is an acid weaker than $HCit^{2-}$. The dissociation constant is given by equation (15·1).

$$\frac{[C_2^{2-}] \times [H^+]}{[C_1^-]} = K_2 \quad \ldots \quad \ldots \quad \ldots \quad (15\text{-}1)$$

where $[C_2^{2-}]$ is the molar concentration of the complex C_2^{2-}. The concentration of citrate being large compared to the cadmium sulphate added, the whole of the cadmium would be present partly as complex C_2^{2-} and partly as C_1^-.

Let x and y be two points on curves (A) and (B) respectively on the same p_H axis. The concentrations of the ions are represented as before. The concentration of hydrogen ion, being the same at x and y, is expressed as $[H^+]$. It can be shown as before that

$$[Ct]_x = [Cit^{3-}]_x \left(1 + \frac{[H^+]}{k_3} + \frac{[H^+]^2}{k_2.k_3} + \frac{[H^+]^3}{k_1.k_2.k_3}\right)$$

or $$[Ct]_x = x\,[Cit^{3-}]_x \quad \ldots \quad \ldots \quad (16)$$

$$[Ct]_y = [C_1^-] + [C_2^{2-}] + x\,[Cit^{3-}]_y$$

or $$[Ct]_y = [CdSO_4] + x[Cit^{3-}]_y \quad \ldots \quad \ldots \quad (17)$$

$$[HCl]_x = [H^+] + [Cit^{3-}]_x \times \left(\frac{[H^+]}{k_3} + 2\frac{[H^+]^2}{k_2.k_3} + 3\frac{[H^+]}{k_1.k_2.k_3}\right)$$

or $$[HCl]_x - [H^+] = y\,[Cit^{3-}]_x \quad \ldots \quad \ldots \quad (18)$$

Since the complex C_2^{2-} is first formed and then with a proton a portion of it is converted to C_1^-.

Total acid liberated at y = $[CdSO_4]$.

$$[CdSO_4] = [H^+] + [C_1^-] + y\,[Cit^{3-}]_y$$

or $$[CdSO_4] - [C_1^-] = [C_2^{2-}] = [H^+] + y\,[Cit^{3-}]_y \quad \ldots \quad (19)$$

From equations (16) and (17) one gets

$$[Ct]_x - [Ct]_y = x\,([Cit^{3-}]_x\,[Cit^{3-}]_y) - [CdSO_4]$$

or $$\Delta[Ct] = x\,\Delta[Cit^{3-}] - [CdSO_4] \quad \ldots \quad \ldots \quad (20)$$

From equations (18) and (19) one gets

$$[HCl]_x - [C_2^{2-}] = y\,\Delta[Cit^{3-}] \quad \ldots \quad \ldots \quad (21)$$

From equations (20) and (21) one gets

$$\Delta[Ct] = \frac{x}{y}\,([HCl]_x - [C_2^{2-}]) - [CdSO_4]$$

or $$\frac{\frac{x}{y}\,[HCl]_x - [CdSO_4] - \Delta[Ct]}{(x/y)} = [C_2^{2-}] \quad \ldots \quad \ldots \quad (22)$$

$[H^+]$, $[HCl]_x$, $[Ct]_x$, $[Ct]_y$ and $[CdSO_4]$ are obtained from the curves in Fig. 3 x/y and $\Delta[Ct]$ are calculated and $[C_2^{2-}]$ is obtained from equation (22). $[C_1^-]$ is obtained by subtracting $[C_2^{2-}]$ from $[CdSO_4]$. The values of K_2, calculated by equation (15-1), are collected in Table III. The average value of the equilibrium constant is 4.86×10^{-9}. The results confirm the assumption that C_2^{2-} is a stronger base, *i.e.*, C_1^- is a weaker acid than $HCit^{2-}$. It is interesting to note that even at p_H 7.5 $[C_1^-]$ is ten times greater than $[C_2^{2-}]$. It is possible to convert the complex into C_2^{2-} by titrating against sodium hydroxide and roughly know the concentration of C_1^- in the solution. The following experiment was done to demonstrate C_1^- behaving as a monobasic acid.

TABLE III

p_H.	x/y.	Δ[Cit] $\times 10^3$.	$[HCl]_x$ $\times 10^4$.	$[CdSO_4]$ $\times 10^3$.	$[C_1^-] \times 10^3$.	$[C_2^{2-}]$ $\times 10^4$.	$K_2 \times 10^9$.
7.50	103.40	1.97	1.992	1.675	1.511	1.641	3.43
7.45	92.32	2.94	3.311	2.531	2.259	2.719	4.27
7.40	82.35	3.65	3.969	3.125	2.810	3.147	4.46
7.35	73.53	4.47	4.624	3.818	3.469	3.496	4.50
7.30	65.60	5.29	5.277	4.490	4.111	3.785	4.62
7.25	58.59	6.08	5.929	5.114	4.712	4.019	4.80
7.20	52.30	6.97	6.580	5.883	5.465	4.180	4.83
7.15	46.77	8.13	7.228	6.898	6.433	4.673	5.14
7.10	41.77	8.89	9.162	7.578	7.057	5.211	5.87
7.00	33 40	11.27	12.350	9.677	9.069	6.084	6.71

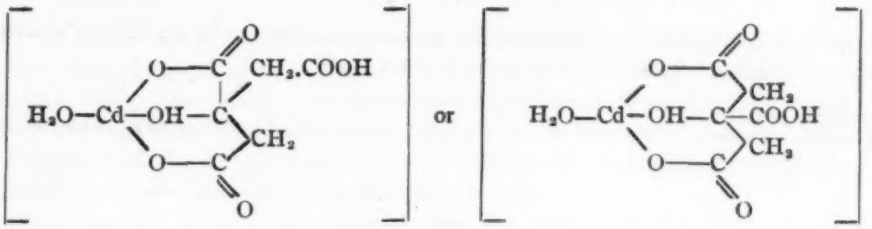
The solution (145 c.c.) containing 0.025 g. mol. of KNO_3, 0.01 g. mol. of sodium citrate and 0.001 g. mol. of cadmium sulphate was titrated against 0.1*N*-NaOH solution. The results are shown in curve (B) in Fig. 4. Curve (A) represents the results obtained with another solution with the same conditions as the previous one except that there is no cadmium sulphate. Curve (B) is very similar to the neutrallsation curve of an acid. It is of interest to note that the neutralisation point is reached at about 11 c.c. of alkali. The p_H attained by the solution containing cadmium due to the addition of 11 c.c. of alkali is reached by the other solution on addition of 1 c.c. of the same alkali ; 10 c.c. of alkali, *i.e.*, 0.001 g. mol. of NaOH is consumed by the complex formed from 0.001 g. mol. of cadmium sulphate.

Structure of the Complex

Fig. 2 indicates that the undissociated carboxyl group in citrate ligand existing at lower p_H are induced to ionise due to the complex formation. No proton is, however, liberated from the hydroxyl group as the two curves converge near about neutralisation point. The results therefore do not indicate whether the hydroxyl group is joined to the central cadmidm atom or not. If the hydroxyl group is not joined to the cadmium atom, the three carboxyl groups of citrate ligand cannot give a complex of sufficient stability as five- or six- membered ring cannot be formed. For the formation of a stable complex the hydroxyl group should be attached to the central atom. The oxygen atom in the

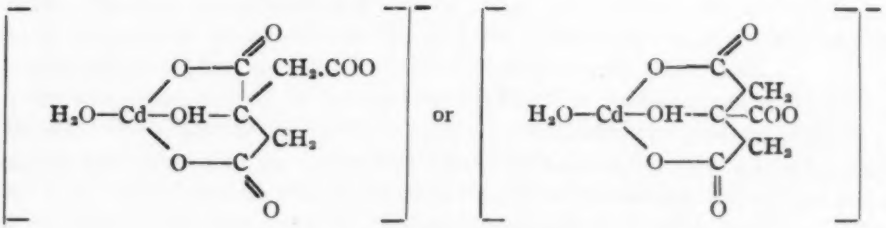
hydroxyl group may donate a pair of electrons even if the proton is not ionised. Probably such a thing happens in the citrate complex of cadmium.

The complex C may be represented by the following structure in which the citrate ligand occupies three co-ordination positions and the fourth position is occupied by a molecule of water, the presence of which is necessary to explain the formation of C_2^{2-}. The co-ordination number of cadmium in complex has been reported to be both four and six. If co-ordination number six is more favoured by cadmium in the citrate complexes, two more water molecules might be present in the structures given below. Two different structures of each complex are probable since the three carboxyl groups of citrate ligand are not similar and it is not possible to predict which of the two carboxyl groups reacts.



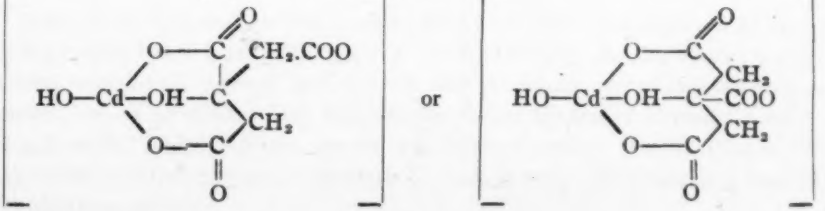
(Complex C)

The carboxyl group in complex C dissociates as the p_H is increased to give C_1^-. The structure of C_1^- may be represented by

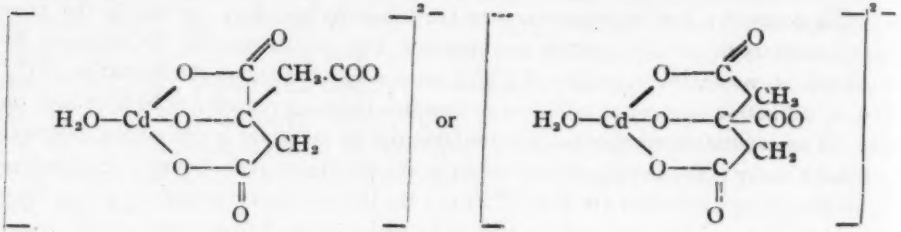


(Complex C_1^-)

The complex C_2^- dissociates above p_H 7 to H^+ and C_2^{2-}. The water molecule present in the co-ordination sphere dissociates. The structure of C_2^{2-} may be represented by



If, however, the proton liberated from C_1^- to give C_2^{2-} comes from the hydroxyl group attached to the cadmium atom, the structure of C_2^{2-} may be represented by



(Complex C_2^{2-})

Sri R.K. Pattanaik, one of the authors, thanks the authorities of the Utkal University for granting him a scholarship to carry on research work.

Department of Chemistry,
Ravenshaw College,
Cuttack-3.

Received November 28, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

HYDRATION OF ALUMINIUM OXIDE SOLS

By A. K. M. Trivedi, K. M. Buch and M. J. Patani

Hydration of micelles in the case of aluminium oxide sols may be obtained by studying the distribution of ammonium ion across a semipermeable membrane. After allowing for the membrane-equilibrium effect, calculated indirectly, it has been found that 25.2 moles of water per mole of aluminium oxide are present in the micelles. An alternative method of obtaining hydration is to determine viscosity at low concentration, calculate hydration according to Einstein's equation and to extrapolate the hydration values so obtained to zero concentration of aluminium oxide. Both the methods provide results of the same order.

The properties of metallic oxide sols are governed by both the charge as well as the solvation of the micelles (Freundlich, "Colloid and Capillary Chemistry", 1926, pp. 521, 625). Such sols are on the border line between hydrophobic and hydrophilic sols. Although aluminium oxide sols are known to be hydrated (Weiser, "Inorganic Colloid Chemistry", Vol. II, 1935, p. 117), it appears that no attempt has been made to measure quantitatively the extent of hydration directly.

One method (Trivedi and Divatia, *Proc. Ind. Acad. Sci.*, 1953, **37A**, 33) whereby the hydration of the micelles may be obtained is to consider the distribution of an electrolyte like ammonium chloride across a semipermeable membrane. The distribution of ammonium ions across a membrane is affected by (*i*) the adsorption of ammonium ions by the micelles, (*ii*) Donnan-membrane equilibrium and (*iii*) hydration of micelles. The first is improbable and may be ruled out. Hence, the distribution of ammonium ion will be affected by (*ii*) and (*iii*). The hydration of the micelles may be obtained provided that one can calculate the membrane-equilibrium effect.

An alternative method of determining hydration is the measurement of viscosity of the sol. Thus, Hatschek (*Kolloid Z.*, 1912, **11**, 280) concluded that the increase in viscosity with dispersion as observed by Óden (Der Kolloide Schwefel", Upsala, 1913, p. 89) in the case of Raffo sulphur sol could be explained by assuming that micelles in the case of sulphur sol were hydrated. For hydrophilic sols Kruyt also observed: "The decrease of $(n_s-n_o)/n_o$ from the point of view of Einstein's equation must be interpreted as the process of desolvation" ("Colloid Science", Part II, 1949, p. 201). The interpretation of viscosity data is, however, beset with considerable difficulties (Freundlich, *loc. cit.*, p. 539).

Experimental

Methods of preparation and analysis of the sols have been reported earlier (Trivedi and Buch, this *Journal*, 1957, **34**, 337). To determine NH_4^+ ion, an aliquot portion of the sol was coagulated, filtered and washed and the filtrate was treated with an excess of standard NaOH solution. The solution was boiled till free of ammonia, cooled, excess of standard HCl added and the excess was titrated against NaOH (Vogel, "A Text Book of Quantitative Inorganic Analysis", 1948, p. 305). The following sols were used for various experiments.

TABLE I

Sol.	Al_2O_3. (in g./litre)	Chloride.	Method.	Hydration (in moles of water per mole of Al_2O_3).
A	30.12	1.418	Membrane equilibrium	25.2
B	19.24	0.460	Viscosity	26.0
C	15.50	0.212	,,	38.0

Membrane Equilibrium.—A partially dialysed sol, admixed with ammonium chloride (far below the C. V.), was kept in collodion bags, suspended in water. After attainment of equilibrium the sol inside (I) and very dilute sol outside (E) the bag were analysed for different constituents. The results of the membrane equilibrium experiments are shown in Table II.

TABLE II

Expt.	Concentration of Al_2O_3 (g./litre).			Conc. of NH_4^+ (m.e./litre).		Apparent density.	S.H.V.
	I.	E.	(I-E).	*X.	E.		
1	26.20	0.120	26.08	54.7	59.6	0.2542	15.7
2	24.92	0.560	24.36	52.1	58.3	0.2276	17.6
3	26.22	0.760	25 46	52.4	60.2	0.1964	20.4
4	26.48	0.400	26.08	53.5	61.6	0.1981	20.2
5	26.20	0.140	26.06	58.8	67.3	0.2070	19.3
6	25.86	0.130	25.73	58.2	66.8	0.2057	19.5

* Calculated as shown below. Mean 18.8

Viscosity.—The viscosity of the sols at different dilutions was determined by Ostwald viscometers at $35 \pm 0.1°$.

DISCUSSION

The aluminium oxide sol was stabilised by aluminium chloride and contained free ammonium chloride added as a reference substance. To calculate hydration effect, it is necessary to estimate the membrane equilibrium effect which, however, cannot be obtained directly. It may be indirectly calculated assuming that 20% of the adsorbed Al^{3+} ions are effective in the membrane equilibrium.

The concentration of adsorbed Al^{3+} ions will be equal to the concentration of the chloride, the counter-ion. Knowing the concentration of chloride-ion per g. of aluminium oxide in the original sol, the concentration of adsorbed ion responsible for the membrane equilibrium can be calculated. An example will make the procedure clear.

The original sol contains 30.12 g./litre of Al_2O_3 and 1.418 g./litre (0.040 g.e./litre) of chloride. Hence, the adsorbed chloride per g. of Al_2O_3 will be $0.040/30.12 = 0.0013$ g.e. of chloride per g. of colloid. In the experiment 1 (Table I) the difference in concentrations of aluminium oxide, inside and outside the membrane, is 26.08 g./litre. Hence, the concentration of adsorbed chloride is $0.0013 \times 26.08 = 0.0339$ g.e./litre, *i.e.* 33.9 m.e./litre. Assuming that 20% of the adsorbed ions are active in membrane equilibrium, the effective concentration of the absorbed ions will be 33.9/5 m.e./litre.

Hence, following Donnan's fundamental relation (Bolam, "The Donnan Equilibria", 1932, p. 4) it can be easily shown that

$$X^2 = (NH_4)_1 \times \left[(NH_4)_1 + \frac{Al^{3+}}{5} \right]$$

where 'X' is the hypothetical concentration of NH_4^+ ion outside the membrane, assuming that the membrane equilibrium effect alone is effective, and $(NH_4)_1$ is the measured concentration of ammonium ions inside the membrane (data not given),

$$\therefore \quad X^2 = 51.4 \times (51.4 + 6.77) \; ; \; X = 54.7 \text{ m.e./litre.}$$

In all cases 'X' was found to be less than the concentration of NH_4^+ ion outside the membrane. This difference is due to hydration of the micelles, *i.e.*, a part of the solvent is immobilised in the colloidal particle. Knowing the value of X, the apparent density, *D*, and specific hydrodynamic volume S.H.V. can be calculated by a procedure similar to the one previously employed (Trivedi and Divatia, *loc. cit.*). Taking the average value of S.H.V. as 18.8 and density of Al_2O_3 as 4.0 g./c.c. (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. V, 1946, p. 265) there will be 17.8 g. of water to 4.0 g. of aluminium oxide or $(17.8/1) \times (102/4) = 25.2$ moles of water per mole of aluminium oxide (M.W. of $Al_2O_3 = 102$).

In membrane equilibrium experiments, apart from the inherent experimental errors involved, selecting 20% of total adsorbed ions as responsible for membrane equilibrium effect is somewhat arbitrary. In the conductivity experiments (Trivedi and Buch, *loc. cit.*) about 0.3 part of the total adsorbed ions is considered free. But the sols used for membrane equilibrium were of lower purity and were likely to contain free $AlCl_3$. The actual concentration of fixed Al^{3+} ion may be somewhat lower and, hence, taking 20% of the total analytically determined ions as responsible for the membrane equilibrium appears to be justified. If 30% of the ions are considered responsible for the membrane equilibrium effect, the hydration value obtained will be about 25% lower. Even the experimental variation in S.H.V. is about 15%. Besides, the value of hydration increases both with purity and concentration. An alternative method of determining hydration in the case of these sols is by determination of viscosity. Knowing the specific viscosity $(\eta_s/\eta_o - 1)$ of the sol and determining the density of the sol as well as of water, it is possible to calculate hydration of micelles at any particular concentration.

In the case of diluted sol B, when the concentration is 3.100 g./litre of Al_2O_3, the relative viscosity is 1.29. If f is the volume of suspended particles (Weiser, "Inorganic Colloid Chemistry", Vol. III, 1938, p. 178),

$$f = \frac{\eta/\eta_o - 1}{k} \text{ where } k \text{ is taken as 2.5 and } \eta/\eta_o = 1.29.$$

$$\therefore f = \frac{1.29 - 1}{2.5} = 0.116.$$

Knowing the density of the sol (d_s) and that of water (d_w), the apparent density (d) of the micelles can be easily obtained (Weiser, *loc. cit.*).

$$d = \frac{d_s - d_w}{f} + d_w$$

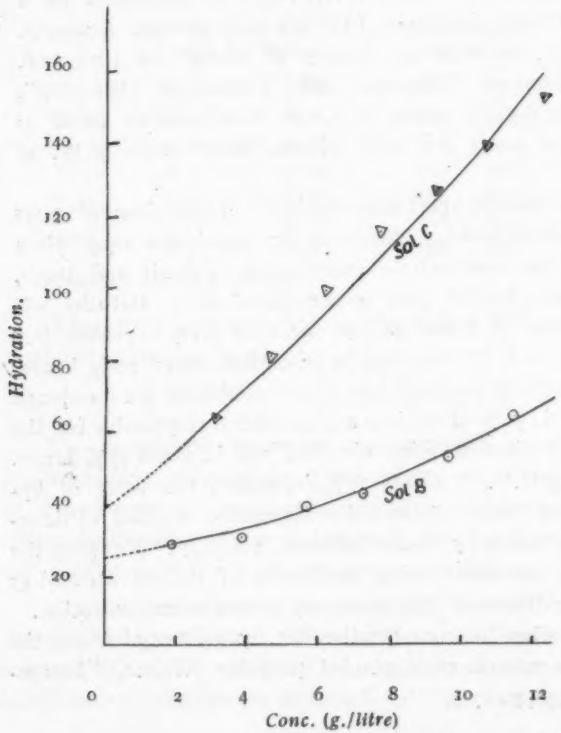
$$\therefore d = \frac{1.0018 - 0.9941}{0.116} + 0.9941 = \frac{0.0077}{0.116} + 0.9941 = 1.06002$$

Assuming 'x' to be the volume fraction of water, $(1-x)$ will be the volume fraction of Al_2O_3 particles. If the density of Al_2O_3 is taken as 4.0 g./c.c. (Mellor, *loc. cit.*), it follows that $0.9941\,x + 4.0(1-x) = 1.06002$.

Solving the above equation, $x = 0.97804$ and $(1-x) = 0.02196$. The molecular weight of Al_2O_3 is 102 and that of water is 18; therefore,

$$\text{Hydration} = \frac{0.9941 \times 0.97804}{18} \times \frac{102}{4.0 \times 0.02196} = 62.3 \text{ moles of water per mole of } Al_2O_3.$$

FIG. 1



The hydration value obtained as above in the case of both the sol may be plotted against concentration. The value of "apparent" hydration increases rapidly with concentration. However, by plotting the values of hydration for lower concentrations and extrapolating them to zero concentration, one may obtain 'real' hydration value. The values come out to be 38 and 26 moles of water per mole of aluminium oxide (see Fig. 1). The rapid increase in viscosity and the 'apparent' values of hydration are due to the non-Newtonian behaviour of the sol at finite concentration. However, extrapolation procedure, as shown above, does yield results which are of the same order as in the membrane equilibrium experiments (see Table I).

From this one may conclude that the viscosity method applied as above is of some use in indicating the order of hydration of micelles in such systems.

Thanks of the authors are due to the Ahmedabad Education Society for a generous grant towards chemicals and apparatus.

CHEMISTRY DEPARTMENT,
L. D. ARTS COLLEGE AND M. G. SCIENCE INSTITUTE,
AHMEDABAD.

Received October 29, 1956.

[J our. Indian Chem. Soc , Vol. 34, No. 9, 1957]

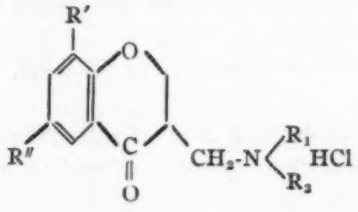
POSSIBLE ANTIAMOEBIC AGENTS. PART III. MANNICH BASES FROM THIOCHROMAN-4-ONES

By A. B. Sen and Yashwant D. Kulkarni

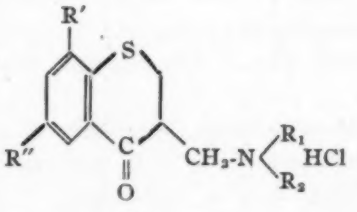
Mannich bases from several substituted thiochromanones have been prepared with a view to testing them for their antiamoebic activity.

Wiley (*J. Amer. Chem. Soc.*, 1951, **73**, 4205) has observed interesting amoebacidal activity in a group of Mannich bases (Ia) derived from substituted chromanones. We have extended this work and reported the syntheses of Mannich bases (Ib) from several chlorochromanones, with a view to studying the effect of chlorine atoms on the amoebacidal activity (this *Journal*, 1957, **34**, 467).

In the present investigation several Mannich bases (II) have been synthesised, for the first time, from substituted thiochromanones with a view to testing them for their antiamoebic activity. The thiochromanone nucleus being isosteric with the chromanone nucleus, the Mannich bases derived from the former are also expected to possess amoebacidal activity.



(I)



(II)

[Ia : R′ and R″ = various groups.]
[Ib : R′ and R″ = chlorine atoms.]

The thiochromanones were prepared from thiophenol, *o*-chloro-, *p*-chloro- and *p*-methyl-thiophenols. Substituted thiophenols required for the work were prepared by the method of Tarbell and Fukushima (Org. Syn. Col. Vol. III, p. 809) using the condensation of diazonium salts of substituted anilines with potassium ethylxanthate and subsequent alkaline hydrolysis of the resulting xanthogenic esters in alcohol.

β-(Thiophenoxy)-propionic acids were prepared most conveniently by following the method of Gresham (*J. Amer. Chem. Soc.*, 1949, **71**, 661) using the condensation of thiophenols (as sodium salt) with β-propiolactone.

Cyclisation of these acids into thiochromanones was best effected by concentrated sulphuric acid (98%). This consisted in dissolving the β-thiophenoxy-acids in 10 parts by weight of sulphuric acid (98%) and allowing the solution to stand at room temperature for 12-24 hours (cf. Krollpfeiffer and Schultze, *Ber.*, 1923, **56**, 1819; 1925, **58**, 1654; Hurd and Hayao, *J. Amer. Chem. Soc.*, 1954, **76**, 5065). In our studies,

we have observed that if these acids are allowed to remain in sulphuric acid for more than 6 hours, the yields of thiochromanones decrease considerably.

For the syntheses of Mannich bases (II) equimolar quantities of a thiochromanone, paraformaldehyde and a secondary or primary amine hydrochloride were heated under reflux for 6 hours in dry benzene as a solvent. The reaction mixture was acidified with 5-10 drops of A.R. hydrochloric acid, at the start of the reaction. In most of the cases, during the reaction, the Mannich bases separated as crystalline solids and did not need any concentration of the solvent for their isolation. Absolute alcohol and 95% alcohol, when substituted as solvents, lowered the yield of the Mannich bases considerably (less than 5%).

All the Mannich bases (II) (as hydrochlorides) were found to be stable. Their aqueous solutions on standing did not decompose and (II) could be isolated on evaporation. The free bases were sticky and low-melting compounds, which were not crystallisable. However, the bases were characterised through their picrates.

Experimental

Thiophenols and β-Thiophenoxypropionic Acids.—The thiophenols, viz., thiophenol, *p*-chloro-, *o*-chloro- and *p*-methyl-thiophenols, required for the work were prepared according to the method of Tarbell and Fukushima (*loc. cit.*). These were converted into the corresponding β-thiophenoxypropionic acids by condensing with β-propiolactone (Gresham, *loc. cit.*).

o-Chlorothiophenol was prepared from *o*-chloroaniline in ~62.5% yield, b.p. 80°/1 mm.

β-(o-Chlorothiophenoxy)-propionic acid was obtained from *o*-chlorothiophenol in 88% yield, m.p. 89-90°. It was recrystallised from ethanol. (Found: S, 14.67. $C_9H_9O_2ClS$ requires S, 14.78%).

Thiochromanones.—The cyclisation of the above β-thiophenoxypropionic acids to thiochromanones was effected with 98% H_2SO_4 (Krollpfeiffer and Schultze, *loc. cit.*). The preparation of 8-chlorothiochromanone is given below.

8-Chlorothiochromanone.—β-(*o*-Chlorothiophenoxy)-propionic acid (5 g.) was dissolved in 98% H_2SO_4 (50 g., cold) with an immediate development of a red coloration. After standing at room temperature for 6 hours, the reaction mixture was poured over crushed ice (200 g.). The solid (4.2 g.) separating was first washed with sodium bicarbonate solution and then with cold water. It was dried and then recrystallised from 50% ethanol, yield 92%, m.p. 86-87°. (Found: S, 15.95. C_9H_7OClS requires S, 16.11%). Its 2:4 dinitrophenylhydrazone melted at 267° (decomp.). (Found: N, 14.63. $C_{15}H_{11}O_4N_4SCl$ requires N, 14.80%).

3-Dialkylamino-alkyl-thiochroman-4-one Hydrochlorides: The Mannich Reaction.—A mixture of the thiochromanone (0.01 *M*) and paraformaldehyde (0.01*M*) in dry benzene (25 c.c.) was heated under reflux for 30 minutes. To this was added 0.01 *M* of a secondary or primary amine hydrochloride (the amines used were dimethylamine, piperidine, morpholine, benzylamine di-*n*-propylamine and piperazine).

TABLE I

Mannich bases (hydrochloride) (II).

Sl. No.	R' & R''.	R_1 & R_2.	M.P.	Yield.	Mol. formula.	% Nitrogen.		% Sulphur.		Picrates			
						Found.	Calc.	Found.	Calc.	M.P.	Mol. formula.	% Nitrogen.	
												Found.	Calc.
1.	H	Piperidyl	176°	67%	$C_{15}H_{20}ONClS$	4.54	4.71	10.48	10.75	153°	$C_{21}H_{22}O_8N_4S$	11.21	11.43
2.	...	Morpholinyl	157°	50	$C_{14}H_{18}O_2NClS$	4.71	4.67	10.35	10.68	128°	$C_{20}H_{20}O_9N_4S$	11.13	11.38
3.	...	Benzyl	168°	71	$C_{17}H_{18}ONClS$	4.31	4.38	10.21	10.01	...	...	...	...
4.	6-Me	Piperidyl	164°	60	$C_{16}H_{22}ONClS$	4.32	4.49	...	...	...	...	...	...
5.	...	Morpholinyl	171°	52	$C_{15}H_{20}O_2NClS$	4.36	4.47	...	...	...	...	...	...
6.	...	Benzyl	188°	80	$C_{16}H_{20}ONClS$	4.30	4.20	...	...	...	...	...	...
7.	...	Dimethyl	157°	75	$C_{13}H_{18}ONClS$	4.70	4.79	11.67	11.78	...	...	...	...
8.	6-Cl	Piperidyl	194°	74	$C_{15}H_{19}ONCl_2S$	4.30	4.22	9.48	9.64	160°	$C_{21}H_{21}O_8N_4ClS$	10.25	10.68
9.	...	Morpholinyl	166°	72	$C_{14}H_{17}O_2NClS_2$	4.01	4.19	9.25	9.58	157°	$C_{20}H_{19}O_9N_4ClS$	10.32	10.64
10.	...	Benzyl	197°	68	$C_{17}H_{17}ONCl_2S$	4.00	3.96	9.10	9.04	...	...	...	...
11.	...	Dimethyl	160°	80	$C_{12}H_{15}ONCl_2S$	4.90	4.79	10.84	10.96	...	...	...	...
12.	8-Cl	Piperidyl	211°	78	$C_{15}H_{19}ONCl_2S$	4.00	4.22	9.54	9.64	164°	$C_{21}H_{21}O_8N_4ClS$	10.32	10.68
13.	...	Morpholinyl	169°	75	$C_{14}H_{17}O_2NCl_2S$	4.20	4.19	9.35	9.58	174°	$C_{20}H_{19}O_9N_4ClS$	10.15	10.64
84.	...	Benzyl	195°	77	$C_{17}H_{17}ONCl_2S$	3.78	3.96	9.21	9.04	...	...	...	...
15.	...	Dimethyl	178°	76	$C_{12}H_{15}ONCl_2S$	4.69	4.79	10.83	10.96	159°	$C_{18}H_{17}O_3N_4ClS$	11.13	11.56
16.	...	Di-*n*-propyl	151°	45	$C_{16}H_{23}ONCl_2S$	...	...	9.15	9.07	...	...	...	...
17.	...	Piperazine	98°	50	$C_{24}H_{26}O_2N_2Cl_4S_2$	4.73	4.83	11.21	11.03	260°	$C_{30}H_{30}O_{16}N_6Cl_2S_2$	11.30	11.60

* Vide structure (VI)

The reaction mixture was acidified with 5-10 drops of A.R. HCl and refluxed for 3-6 hours, during which most of the Mannich bases separated in crystalline forms. After cooling, the reaction mixture was filtered and the product obtained was washed with dry benzene and finally recrystallised from absolute alcohol.

The compounds (as HCl salts) are mostly soluble in hot water (excepting the products from benzylamine) and are very stable. The intense and bright red colour with a drop of H_2SO_4 (conc.) is the most characteristic property of all the Mannich bases reported in the present work. The Mannich bases (II) were characterised by preparing their picrates.

Picrates.—The compound (II: 0.05 g.) was dissolved in hot water (10 c.c.) and mixed under shaking with a saturated aqueous solution of picric acid (10 c.c.). An immediate turbidity appeared and crystalline picrates separated on cooling. These were filtered and purified by recrystallisation from ethanol.

Decomposition of the Products.—The compounds (8,9 and 13 of Table I) was dissolved in water (10 c.c.) separately. After standing at room temperature for 24 hours, 1 g. each of the original products separated, showing no indication of decomposition. The melting points and analyses of the Mannich bases and their picrates are shown in Table I.

CHEMICAL LABORATORIES,
LUCKNOW UNIVERSITY,
LUCKNOW.

Received April 15, 1957.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

AN ANALYSIS OF THE NEUTRALISATION CURVES OF THE COLLOIDAL ACIDS. PART III

By S. L. Gupta

The neutralisation curves of two colloidally dispersed resins (resorcinol-formaldehyde resin and Amberlite IR 100) have been analysed theoretically, following the model and the line of analysis described earlier.

In our previous communications (Gupta, Parts I and II, this *Journal*, 1956, **33**, 587 ; 1957, **34**, 63), we suggested a model for the colloidal polybasic acids and also proposed a method for constructing the polybasic acid curve by evaluating a series of dissociation constants and corresponding acid values. It was shown that the titration curve of the polybasic acid of the dimension of colloidal particles could be interpreted as the neutralisation of a series of monobasic acids with drifting dissociation constants. The idea is that at the beginning of a titration, only the strongest and a small fraction of the total intermicellar acidity with a correspondingly high value of the dissociation constant is active, just as in oxalic acid or in phosphoric acid solutions only one-half or one-third respectively of the total acidity is active at the beginning. As this acid is neutralised further dissociation takes place from the surface of the colloidal acid with a corresponding shift in the dissociation constant. In the case of common polybasic acids in true solution, say a dibasic acid of the formula H_2R, the equilibriums are

$$H_2R \rightleftharpoons H^+ + HR^- \quad \text{and} \quad HR^- \rightleftharpoons H^+ + R^{2-},$$

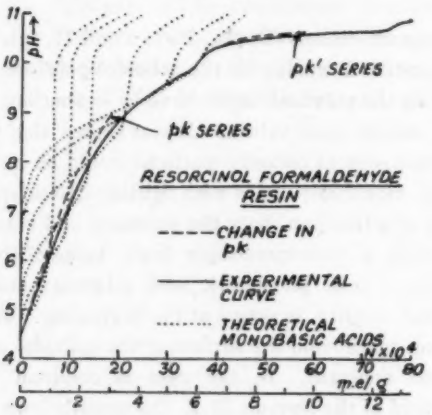
and one gets two dissociation constants for the two types of ions produced, *e.g.*, HR^- and R^{2-}. In the case of the colloidal acids, however, we have assumed that each dissociation from the surface produces an ion R^-, *i.e.*, we are concerned with only one equilibrium, and a number of such ions are just connected together on the surface of the colloidal particles. This happens because contiguous groups are not successively ionised. As the anions, produced from the neutralisation of the strongest fraction, are not different from those produced by the subsequent ionisation, the only observable change is an increase in the total active acidity with a corresponding decrease in the dissociation constant, the curve continuing to remain monobasic. Thus, for colloidal acids containing one type of group, one may expect a series of increasing active acidities with correspondingly diminishing dissociation constants. If the intermicellar groups are themselves dibasic or if the groups are of different types with widely separated dissociation energies, then one may expect two series of such dissociation constants. In that case the titration curve shows a break or an inflection point. In the analysis of the titration curve of the colloidal resorcinol-formaldehyde resin, that follows, one comes across such a situation.

In each of the resorcinol units of the resin structure of the resorcinol-formaldehyde resin there are two −OH groups which are separated from each other by a fixed distance *i.e., meta* to each other in the benzene ring, while the resorcinol units are distributed at random throughout the resin. Consequently the distribution of the −OH groups in a resin particle occurs at random but in pairs and in the case of the titration of this colloidal resin in its H-form, one may expect two series of drifting dissociation constants.

Resorcinol-formaldehyde Resin

The preparation of the acid-catalysed resorcinol-formaldehyde resin, the isolation of the colloidal fraction in its H-form and its titration have been reported earlier (Gupta, this *Journal*, 1956, **33**, 90). The experimental curve is shown in Fig. 1. The sus-

FIG. 1



pension had a colloid content of 0.58 g./litre. As the initial flat run, indicative of ion adsorption, is absent, the acid may be taken to be wholly intermicellar (cf. Case B, Part I, *loc.cit.*). Also preliminary experiments showed that the resin did not adsorb ions unless it was at a very high p_H. In the case of a monobasic acid HR dissociating into H^+ and R^- ions, one gets

$$a_{Na}{}^{+} = a_{R}{}^{-} + a_{OH}{}^{-} - a_{H}{}^{+}$$

or

$$b = \frac{Ck}{k + x} + \frac{K_w}{x} - x \qquad \ldots (1)$$

where 'b', 'C', 'k', 'K_w' and 'x' have their usual significances. Rearranging,

$$Ck = \left(b - \frac{K_w}{x} + x\right)(k + x) \qquad \ldots (2)$$

By applying this equation to the values obtained by interpolation from the smooth curve and treating the product 'Ck' as constant over short ranges, 'k' can be solved from two consecutive values of 'Ck'. Substitution of the value of 'k' in equation (2) affords the value of 'C'. The results are shown in Table I.

TABLE I

No. of points selected.	'b'$\times 10^4$.	p_H.	Ck (by eq. 2).	k.	pk.	C.
1	2.3 N	5	2.4×10^{-4} ($k+1\times10^{-5}$)	6×10^{-6} (k_1) from (1) & (2)	5.22	6.416×10^{-4}(C_1)
2	5.5	6	5.5×10^{-4} ($k+1\times10^{-6}$)	1.2×10^{-6} (k_2) from (2) & (3)	5.92	10.07×10^{-4}(C_2)
3.	9.3	7	9.3×10^{-4} ($k+1\times10^{-7}$)	1.89×10^{-7} (k_3) from (3) & (4)	6.72	14.21×10^{-4}(C_3)
4.	13.5	8	13.5×10^{-4} ($k+1\times10^{-8}$)	1.54×10^{-8} (k_4) from (4) & (5)	7.94	22.25×10^{-4} (C_4)
5.	21.0	9	20.9×10^{-4} ($k+1\times10^{-9}$)	1.95×10^{-9} (k_5) from (5) & (6)	8.71	31.61×10^{-4}(C_5)
6.	27.5	9.5	27.2×10^{-4} ($k+1\times10^{-9.5}$)	9.84×10^{-10} (k_6) from (6) & (7)	9.01	36.1×10^{-4} (C_6)
7.	31.0	9.75	30.44×10^{-4} ($k+1\times10^{-9.75}$)			

It will be seen from the fifth and seventh columns of the table that as the 'C' values increase, the 'k' values diminish. The theoretical curves for the 'C' values with corresponding dissociation constants have been constructed using equation (1) and shown by the dotted lines in Fig. 1. The middle points (approx.) of all such curves joined by the dashed line show the smooth change in pk value throughout the titration up to the first equivalence point, *i.e.*, neutralisation of one $-$OH group per resorcinol unit. As the experimental values may not be very accurate at the high p_H, we have not calculated the values for the second series (pk' series). The maximum neutralisable acidity found is 1220 m.e./100 g. of the oven-dried resin (105°) which is the theoretical value on the assumption that the $-$OH groups are hydrated with one molecule of water at that temperature (Gupta, this *Journal*, 1956, **33**, 90).

In our previous analyses for the silicic acid sols and clay systems (Parts I and II, *loc.cit.*), we have indicated these different 'C' and 'k' values by (C_1, k_1), (C_2, k_2) etc., while, in fact, the change from one set of values to the next is continuous. It will be seen from Fig. 1 that the experimental curve passes through those points where a lower value of the active acidity with a higher value of the dissociation constant tends to deflect the curve to the right, while a higher value of the active acidity with a lower value of the dissociation constant tends to deflect the curve to the left of the experimental curve. The experimental curve represents the mean course and is necessarily so for a continuous change in active acidity and dissociation constant. The oscillations will vanish by selecting closer points for evaluation.

Amberlite IR 100 *

The resin was wet-ground in an agate mortar and the fine fraction remaining above a height of 10 cm after 8 hours of undisturbed settling was syphoned off and collected

* This resin was obtained by the courtesy of Messrs. Rohm and Haas Company, Philadelphia, Pennsylvania, U. S. A., through Dr. S. K. Mukherjee, Reader in Applied Chemistry, Calcutta University, for experimental purposes.

in $N/20$-HCl medium. This was then filtered through a sintered glass cruicible, washed free from HCl and resuspended in double distille water. The colloid content was determined (1.98 g./litre) by drying at 105-10°. The neutralisation curve obtained is shown in Fig. 2.

In Amberlite IR 100, one gets an entirely different picture. The resin adsorbs ions and consequently the total acidity is partly micellar and partly intermicellar (cf. Case C, in Part I, *loc. cit.*), *i.e.*, $C_a + C_i$. The intermicellar groups are again of two types *i.e.*, the $-CH_2SO_3H$ groups and the phenolic $-OH$ groups (Kunin and Myers, "Ion Exchange Resins", 1950, p. 58), *i.e.*, $C_i = (C-_{CH_2SO_3H})_i + (C-_{OH})_i$. The intermicellar $-CH_2SO_3H$ groups being strongly ionisable are completely ionised and behave as any soluble strong acid and are the first to be neutralised simultaneously with ion adsorption, while the intermicellar phenolic $-OH$ groups being weakly ionisable are neutralised subsequently as a polybasic acid, being represented by a series of monobasic acids, C_1, $C_2 \ldots C_n$ with drifting dissociation constants, k_1, $k_2 \ldots k_n$, such that $C_n = (C-_{OH})_i$. Consequently, the initial stretch is given by

$$b = C_a + (C-_{CH_2SO_3H})_i + \frac{C_1 k_1}{k_1 + x} + \frac{K_w}{x} - \frac{x.\,C_a}{(C-_{CH_2SO_3H})_i + \frac{C_1 k_1}{k_1 + x} + \frac{K_w}{x}} - x \quad (3)$$

and by

$$b = C_a + (C-_{CH_2SO_3H})_i + \frac{C_2 k_2}{k_2 + x} + \frac{K_w}{x} - x \quad \ldots (4)$$

etc. for subsequent stretches.

The analysis has been made in the following lines. The initial p_H gives the value of $(C-_{CH_2SO_3H})_i$ as due to the presence of these strongly ionisable groups on the surface of the resin particles the dissociation of the phenolic $-OH$ groups, $(C-_{OH})_i$, remain almost suppressed. The initial p_H recorded is 3 8, and consequently, we have assumed $(C-_{CH_2SO_3H})_i$ to have a value of $1.58 \times 10^{-4}N$. The final inflection signifying the end of titration is not very sharp and therefore there may be some uncertainty about the actual value of $(C-_{OH})_i$, but the phenolic slope to the right of the line AB is unmistakable. The micellar acidity, C_a, calculated over the whole suspension is evaluated at $30.92 \times 10^{-4}N$.

As in resorcinol-formaldehyde resin, we have calculated the different C and k values from the slope of the curve to the right of the line AB, which are given below in Table II. The final value, *i. e.*, C_5 has been taken to be equal to $(C-_{OH})_i$.

TABLE II

C ...	$3.86\times10^{-4}(C_1)$	$4.28\times10^{-4}(C_2)$	$5.14\times10^{-4}(C_3)$	$6.84\times10^{-4}(C_4)$	$12.0\times10^{-4}(C_5)$
k ...	$1.84\times10^{-6}(k_1)$	$1.40\times10^{-6}(k_2)$	$3.50\times10^{-7}(k_3)$	$2.71\times10^{-8}(k_4)$	$1.00\times10^{-9}(k_5)$

Thus assuming any value of 'x', the corresponding 'b' value can be obtained by using equations (3) and (4). The theoretical curve, PMQN, is shown in Fig. 2., and the results of analysis are shown in Table III. Also $(a_{Na}$ t any p_H is given by

$$(a_{Na^+})_f = (C_{-CH_2SO_3H})_f + \frac{C_1k_1}{k_1+x} + \frac{K_w}{x} - x \quad \ldots \quad \ldots \quad (5)$$

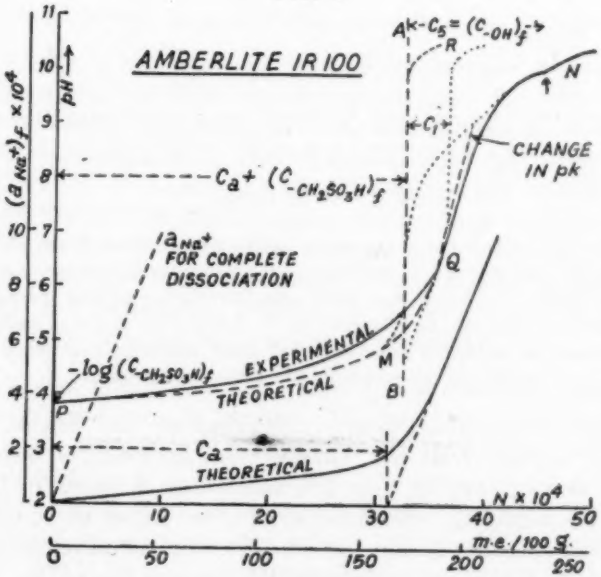
for the initial stretch and replacing (C_1, k_1) by C_2, k_2) etc. for other stretches.

TABLE III

p_H	3.8	4.0	5.0	5.5	6.5	7.5	8.5	9.5
$b \times 10^4$	0.0	12.82	31.59	33.56	36.0	37.22	38.64	41.62
$(a_{Na^+})_f \times 10^4$	0.0	0.65	2.08	2.97	5.08	6.30	7.72	10.70
$(a_{Na^+})_a \times 10^4$	0.0	12.17	29.51	30.59	30.92	30.92	30.92	30.92
			C_1k_1		C_2k_2	C_3k_3	C_4k_4	C_5k_5

It will be seen that the curves are nearly coincident. The slight discrepancy may be due either to non-attainment of equilibrium or to ion specificity that is frequently observed in these systems. The curve PQR shows approximately what the curve could have been if the phenolic $-OH$ groups were not present in the resin system and the intermicellar acidity were made up of only methylenesulphonic acid groups.

FIG. 2



The figure also shows a plot of $(a_{Na^+})_f$ against 'b', *i. e.*, C_{NaOH}. The experimental curves for p_H and a_{K^+} obtained by Marshall and Upchurch (*J. Phys. Chem.*, 1953, **57**, 618) in the case of the titration of Amberlite IR 120, a nuclear sulphonic acid resin, strongly resemble these curves except for the fact that the p_H curve of Amberlite IR 120 appears to be one unit lower. If the p_H curve is raised by slightly more than one unit of p_H, as a whole, then it will fit completely with our method of calculation. That

the p_H curve is to be raised can be shown from the fact that at $p_H = 3$ ($a_H^+ = 1 \times 10^{-3}$ N), $a_K{}^+ = 0$ and at about $p_H = 4$ ($a_H{}^+ = 1 \times 10^{-4}$ N), the $a_K{}^+ \simeq 0.5 \times 10^{-4}$ N as observed from the curves ; consequently with the disappearance of 9×10^{-4} equivalents of H^+ ions we are getting only 0.5×10^{-4} equivalent of K^+ ions in the intermicellar solution. For the neutralisation of any acidic suspension, weak or strong, the concentration of the cation of the added base will always exceed or at least be approximately equal to the H^+ ions disappearing from the solution, and this can only happen by raising the p_H curve as a whole.

The author's thanks are due to Dr. S. K. Mukherjee, Reader in Applied Chemistry, for his continued interest in the work and to Prof. P. B. Sarkar, Head of the Department of Chemistry, for the constant encouragement received.

CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA

Received July 11, 1956.

AN ANALYSIS OF THE NEUTRALISATION CURVES OF THE COLLOIDAL ACIDS. PART IV

BY S. L. GUPTA

The features of the conductometric titration curves of the colloidal acids have been discussed with reference to our previous theoretical findings on the features of the potentiometric titration curves. The changes such titration curves undergo, when a diacidic base is used for titrating the colloidal acid instead of a monoacidic base, have been brought out. An attempt has also been made to show the extent of agreement between our method of calculation and some published experimental informations on the neutralisation of colloidal AgI sols with hydrogen as the counter-ions.

Conductometric Titration Curves.—The nature of the potentiometric titration curves of the colloidal acids has already been analysed in detail (Gupta, this *Journal*, 1956, **33**, 587; 1957, **34**, 63). The assumptions involved in the deduction of the equations representing potentiometric titration curves of particular shapes necessarily and simultaneously fix up conductometric titration curves of definite and corresponding patterns. It has been assumed that only the free ions and the colloidal particles are the carriers of electricity and the adsorbed ions do not contribute to the conductivity under normal field strength used in the conductivity measurements. Under such circumstances, the expected nature of the specific conductivity-concentration curves will be exhibited by curves A′, B′ and C′, corresponding to potentiometric curves A, B and C in Fig. 1., and by A′ and B′ to those corresponding to A and B in Fig. 2, respectively. A brief description of the theoretical curves shown in Figs. 1 and 2 is given below.

FIG. 1

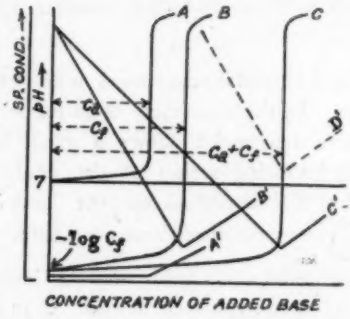
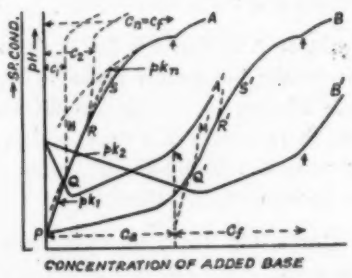


FIG. 2



Curve B in Fig. 1 presupposes that the active groups on the surface of the colloidal acids are strongly ionisable and wholly intermicellar, *i.e.*, there is no ion adsorption (cf. Fig. 1 , Part I, *loc. cit.*). This condition implies a behaviour almost identical with that obtained from any soluble strong acid, the initial p_H corresponding to the total acidity present in the suspension. The monovalent alkali metal ions simply replace the free H^+ ions and, consequently, the expected nature of the conductivity curve (curve B′) is identical with that obtained in the neutralisation curve of any strong acid.

Curve C in Fig. 1 shows the potentiometric neutralisation curve of colloidal acids with strongly ionisable groups with ionsadsorbing properties, *i.e.*, the active groups are partly micellar and partly intermicellar. As the adsorbed ions do not contribute to the conductivity, the neutralising branch of the specific conductivity curve becomes flatter as in C′ in Fig. 1. If it is supposed that the intermicellar acidity in C is equal to the total acidity present in B, then the curves will start from the same point and the total drop in the conductivity in C′ will be the same as occurs in B′. This means that the drop in B′ has simply been spread out in C′. The end-point indicates neutralisation of both micellar and intermicellar acidities and the subsequent slope is identical with what is obtained when alkali is added to neutral salt solutions.

Curve A in Fig. 1 shows the neutralisation of an imaginary colloidal suspension where the active groups are wholly micellar. The intermicellar H^+-ion concentration is due simply to the dissociation of water molecules. Thus, the p_H curve starts from 7. The initial conductivity in A′ is therefore negligibly small, *i. e.*, equivalent to that present in the conductivity water. The addition of alkali does not raise the conductivity significantly until the end-point is reached bacause the competition due to small concentration of H^+ ions in the intermicellar solution is evidently very weak in this stretch, and most of the added cations of the base are exchanged for H^+ ions and adsorbed in the micellar positions. When the neutralisation of the micellar acidity is complete, the curve rises up as when alkali is added to pure water.

Curve D′ in Fig. 1 shows what the specific conductivity curve would have been if the acidity in C were wholly intermicellar, *i. e.*, in that case both the branches of D′ would be parallel to B′ with the height of the point of intersection of the two branches

slightly raised due to higher concentration of the cations in the intermicellar solution and of the colloid anionic constituents on the surface of the colloidal particles (cf. Kruyt, "Colloid Science", Vol. I, 1952, p, 239, Fig. 25).

Curve A in Fig. 2 is due to the neutralisation of a colloidal suspension with wholly intermicellar but weakly ionisable functional groups. In this case there is no ion adsorption. The corresponding specific conductivity curve (curve A′) shows a small initial drop, characteristic of a weak acid, a flat run due to buffering action of the neutralisation curve and finally another bend, signifying end of the neutralisation, the final slope corresponding to the alkali line. These curves therefore consist of three segments.

Curve B in Fig. 2 shows the neutralisation of colloidal acids with weakly ionisable groups and with built-in micellar acidity, *i. e.*, with ion-adsorping capacities. As in C′ in Fig. 1, here also the small initial drop spreads out in B′ due to simultaneous ion adsorption. The rest of the curve B′ is identical with that of curve A′. An experimental verification of this type of curve was published in the case of a clay sol (Sol C) in Part II (*loc. cit.*).

A comparison between curve C′ in Fig. 1 and curve B′ in Fig. 2 shows that there is an extra buffering portion between the two extreme branches in the latter curve, due to the weak acid buffering in the corresponding potentiometric curve. Theoretically, by gradually diminishing the extent of buffering, C′ in Fig. 1 can be obtained from B in Fig. 2. The middle stretch of curve B′ in Fig. 2 in that case will reduce to the point of intersection of the two branches in curve C′ in Fig. 1. The smaller the buffering, the smaller is the length of the middle portion of the specific conductivity curve. This can be seen from the alkali-titration curves of the three AgI sols with hydrogen as counter-ions (De Bruyn and Overbeek, *Kolloid Z.*, 1938, **84**, 186, Figs. 2a, 2b and 7). This also shows that the method of preparation of the colloidal acids has also a large say on their performances.

Neutralisation Curves with Alkaline Earth Hydroxides

The expression for the Donnan equilibrium between micellar and intermicellar solutions in the case of bivalent cations of the titrating base, say Ba^{2+}, may be represented by

$$\frac{\sqrt{(a_{Ba^{2+}})_i}}{(a_{H^+})_i} = \frac{\sqrt{(a_{Ba^{2+}})_a}}{(a_{H^+})_a}$$

by analogy, because it is difficult to deduce an equation for the bivalent ions by rigorous calculations considering each aggregate unlike what obtains in the case of monovalent ions. The above equation is, however, sufficiently exact if the micellar acidity is considered as a whole as one unit. Substitution from the electroneutrality relationships in the above equation gives corresponding relationships as were obtained in the case of alkali metal ions (Part I, *loc. cit.*).

In the case of the titration of a colloidal acid, where the functional groups are strongly ionisable with ion-adsorbing capacities, corresponding to case C, (*a*), in Part I (*loc. cit.*), and to the potentiometric curve C in Fig. 1, remembering,

$$(a_{H^+})_f = x,\ 2(a_{Ba^{++}})_f = C_f + \frac{K_w}{x} - x,\ 2(a_{Ba^{++}})_a = b - C_f = \frac{K_w}{x} + x$$

and

$$(a_{H^+})_a = C_a - b + C_f + (K_w/x) - x$$

one gets by substitution in the Donnan relationship and simplification

$$b = C_a - \frac{x\sqrt{4C_a(C_f + \frac{K_w}{x} - x) + x^2} - x^2}{2(C_f + \frac{K_w}{x} - x)} + C_f + \frac{K_w}{x} - x \qquad \ldots \quad (1)$$

where $2(a_{Ba^{++}})_a$ is given by the first two terms and $2(a_{Ba^{++}})_f$ by the last three terms of the right hand side of the above equation. The corresponding relation for the monoacidic bases, say NaOH, already deduced (Part I, *loc. cit.*), is

$$b = C_a - \frac{x.C_a}{C_f + \frac{K_w}{x}} + C_f + \frac{K_w}{x} - x \qquad \ldots \qquad \ldots \quad (2)$$

where $(a_{Na^+})_a$ and $(a_{Na^+})_f$ are given respectively by the first two terms and the last three terms of the right hand side of equation (2). As usual, the specific conductivities (κ) in the two cases are given by

$$\kappa = \frac{U_{H^+}(a_{H^+})_f + 2U_{\frac{1}{2}Ba^{++}}(a_{Ba^{++}})_f + V_{OH^-}(a_{OH^-})_f + V_{R^-}(2a_{Ba^{++}} + a_{H^+} - a_{OH^-})_f}{1000}$$

and

$$\kappa = \frac{U_{H^+}(a_{H^+})_f + 2U_{Na^+}(a_{Na^+})_f + V_{OH^-}(a_{OH^-})_f + V_{R^-}(2a_{Na^+} + a_{H^+} - a_{OH^-})_f}{1000}$$

where the symbols have their usual significances.

A concrete numerical example will help to clear the position. The values in the following example have been chosen in such a way that the results approach the experimental curves of Van Os, reported by Kruyt ("Colloid Science", Vol. I, 1952, p. 179, Figs. 42 and 43), as closely as possible. Supposing in a colloidal acid suspension with strongly ionisable groups, we have the values: $C_f = 1.3 \times 10^{-4}N$, $C_a = 7.4 \times 10^{-4}N$, and $K_w = 10^{-14}$ then the total colloidal acidity becomes $C_f + C_a = 8.7 \times 10^{-4}N$. The following limiting values of the equivalent conductivities at 18° have been assumed for the different ionic species: $U_{H^+} = 315.2$, $U_{Na^+} = 43.16$, $U_{\frac{1}{2}Ba^{++}} = 55$ and $V_{OH^-} = 173.8$ ohms^{-1}cm^2, together with an arbitrary value of 20 ohms^{-1}cm^2 for V_{R^-}, *i.e.*, for the charge on the intremicellar surface of the colloidal particles. Assuming any value of 'x', *i.e*, $(a_{H^+})_f$, the corresponding values of 'b', $(a_{Na^+})_f$, $(a_{Na^+})_a$, $(a_{Ba^{2+}})_f$ $(a_{Ba^{2+}})_a$, $(a_{OH})_f$ and κ can be calculated by evaluating the terms of the equations (1) and (2). The results are shown in Tables I and II. The theoretical potentiometric curves (b-p_H) and conductometric curves (b-κ) are shown in Fig. 3.

TABLE I

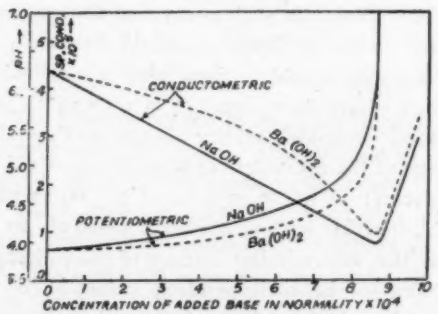
p_H	3.886	4.0	4.5	5.0	6.0	8.0	9.0	10.0
$(a_{H^+})_t \times 10^4$	1.3	1.0	0.316	0.1	0.01	(negligible.)		
$(a_{OH^-})_t \times 10^4$	(negligible)					0.01	0.1	1.0
$(a_{Na^+})_t \times 10^4$	0.0	0.3	0.984	1.2	1.29	1.31	1.4	2.3
$(a_{Na^+})_a \times 10^4$	0.0	1.707	5.6	6.83	7.343	7.4	7.4	7.4
$b \times 10^4$	0.0	2.007	6.584	8.03	8.633	8.71	8.8	9.7
$\kappa \times 10^5$	4.35	3.54	1.68	1.09	0.85	0 84	1.03	2.99

TABLE II

p_H	3.886	4.0	4.5	5.0	6.0	8.0	9.0	10.0
$(a_{H^+})_t \times 10^4$	1.3	1.0	0.316	0.1	0.01	(negligible.)		
$2(a_{OH^-})_t \times 10^4$	(negligible)					0.01	0.1	1.0
$2(a_{Ba^{2+}})_t \times 10^4$	0.0	0.3	0.984	1.2	1.29	1.31	1.4	2.3
$2(a_{Ba^{2+}})_a \times 10^4$	0.0	3.827	6.582	7.156	7.38	7.4	7.4	7.4
$b \times 10^4$	0.0	4.127	7.566	8.356	8.67	8 71	8.8	9.7
$\kappa \times 10^5$	4.35	3.57	1.8	1.24	1.00	1.00	1.20	3.26

The shape of the curves bears a striking resemblance to the potentiometric and conductometric titration curves with caustic alkali, obtained by De Bruyn and Overbeek (*loc. cit.*, cf. Fig. 7), in the case of an AgI sol with hydrogen as the counter-ions and specially to the specific conductivity curves with NaOH and $Ba(OH)_2$, obtained by Van Os (*loc. cit.*), for the same sol. The small weak acid-buffering in the above mentioned potentiometric titration curve of De Bruyn and Overbeek suggests that the acid colloidal AgI sols, though fairly strong, are not comparable to mineral acids in the dissociating powers of their intermicellar acidic groups, *i. e.*, H-I (Ag-I) on the surface of the AgI lattice of the colloidal particles, in this case. Consequently, instead of a sharp point signifying the end of neutralisation in the specific conductivity curve, a very small middle flat portion has been obtained in their experiments, as well as in those of Van Os.

FIG. 3



The $Ba(OH)_2$ curve of Van Os shows a greater amount of drop in specific conductiytiv at the end-point than that obtained with NaOH. This has been possible because

the Ba^{2+} ions in the intermicellar solution have an agregating effect on colloidal suspensions which produce a slight diminution in the value of C_f and increase in the value of C_a by a corresponding amount towards the end-point. This happens with gradual accumulation of Ba^{2+} ions in the intermicellar solution, *i.e.*, with increase of $(a_{Ba^{2+}})_f$. The same thing was also observed in the case of the potentiometric titration with $Ba(OH)_2$ of a clay sol sol, C_1, to which we have already referred in Part II (*loc. cit*). Changes in the state of aggregation during $(a_{Ba^{2+}})$ titration can produce large changes in the features of the titration curves, which we shall have occasion to deal with in detail, in our future communications.

Incidentally, the conductometric titration curves of a sulphur sol with H^+ ions as the counter-ions, described by Pauli (*J. Coll. Sci.*, 1947, **2**, 33), which have the same features as the AgI hydrosols, may be analysed analogously.

The author acknowledges his indebtedness to Dr. S. K. Mukherjee, Reader in Applied Chemistry, and to Prof. P. B. Sarkar, Head of the Department of Chemistry, Calcutta University, for the constant encouragement received.

Department of Chemistry,
University College of Science and Technology,
Calcutta.

Received July 18, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

VISCOSITY OF POLY-2-VINYLPYRIDINE IN ACETIC ACID

By Bimal Bandhu Mukherjee and Mihir Nath Das

Viscosities of poly-2-vinylpyridine have been measured in glacial and aqueous acetic acid media. The reduced viscosity *versus* concentration graphs are typical of a polyelectrolyte. Addition of pyridine, sodium acetate and barium acetate decreases the viscosity. Even small amounts of water exert considerable influence on the viscosity and thereby introduce uncertain factors in the observed results.

Poly-2-vinylpyridine has been found to exhibit polyelectrolytic properties in nitromethane (Cashin, *J. Coll. Sci.*, 1951, **6**, 271) due to the weakly acidic properties of this solvent which enhance the base strength of the polymer. The present paper reports the results of viscosity measurements of poly-2-vinylpyridine in acetic acid in which the polymer is found to exhibit the essential characteristics of a polyelectrolyte. This is perhaps not surprising in view of the fact that in a strongly acidic solvent like acetic acid, the polymer base should be present to a great extent as its salt, polyvinylpyridinium acetate, which by ionisation could logically be expected to behave as a polyelectrolyte. An essentially similar phenomenon has also been observed with solutions of polyamides in formic acid (Schaefgen and Trivisonno, *J. Amer. Chem. Soc.*, 1951, **73**, 4580 ; 1952, **74**, 2715).

Experimental

Two samples (A & B) of poly-2-vinylpyridine were used in the present work. These samples were obtained by bulk polymerisation at room temperature and were purified by dissolving in methylethyl ketone and precipitating with petroleum ether (Maclay and Fuoss, *J. Poly. Sci.*, 1951, **6**, 511). The process was repeated thrice and the brown precipitate finally obtained was dried. A standard solution of this polymer in glacial acetic acid was made in a well-stoppered flask. Measurements were done with this solution with necessary dilution. Two such stock solutions were made with samples A and B respectively.

Materials.—99.5% Acetic acid was distilled using a long fractionating column and the central fraction was collected. A highly purified sample was obtained by freezing the acid sample three times and collecting about 200 c.c. out of one litre of the original sample. Fused sodium acetate was purified by melting and was preserved in well-stoppered bottles. Pyridine was dried over sodium hydroxide beads and then distilled, the central fraction being collected. Barium acetate was prepared by treating pure barium hydroxide with excess of acetic acid and evaporating to dryness. The concentrations of stock solutions of sodium acetate and of pyridine in acetic acid were checked by titration with standard $HClO_4$ in the same solvent, using methyl violet as indicator. Conductivity water was used for all the measurements.

Measurements.—All viscosity measurements were done at 35° (± 0.01°) with two Ostwald viscometers with flow times of 330 and 480 seconds respectively with glacial acetic acid.

TABLE I

Viscosities of poly-2-vinylpyridine.

Conc. (g./100 c.c.)	η_{sp}/C in		Conc. (g./100 c.c.)	η_{sp}/C in	
	Gl. acetic acid Sample A.	Gl. acetic acid +0.3% Ac_2O.		Gl. acetic acid. Sample B.	Gl. acetic acid + 0.3% Ac_2O.
0.10	11.75	7.90	0.10	18.89	10.40
0.05	11.35	9.30	0.07	17.90	...
0.03	12.50	11.10	0.05	17.50	11.70
0.02	13.35	12.00	0.03	19.00	...
0.01	15.90	14.70	0.02	22.30	14.40
0.005	20.10	...	0.01	26.20	15.90
		...	0.005	...	20.10
		...	0.002	...	39.10

Conductance measurements were done at 35° with a direct reading bridge of the philoscopic type using cell voltage of 2.0 at 1000 cycles per second. The conductiviiy cell used had a cell constant of 0.2288.

TABLE II

Conductance in glacial acetic acid.

Conc.	Sp. conductance. Samp'e B.	Equiv. conductance.
0.470 g./100 c.c.	24.88×10^{-6} mho	55.62×10^{-3} mho
0.313	17.35	58.17
0.202	12.33	63.77
0.135	8.86	69.04
0.090	6.05	71.16
0.060	4.34	76.01

TABLE III

Effect of water on viscosity.

Conc.	η_{sp}/C in acetic acid + added water.		
	5% H_2O.	10% H_2O.	20% H_2O.
	Sample B.		
0.10 g./100 c.c.	17.85	16.70	14.80
0.07	...	16.18	14.10
0.05	17.27	...	...
0.04	...	14.60	13.05
0.03	16.50	14.16	12.90
0.02	...	13.80	12.35
0.01	17.19	13.50	11.75
0.005	17.13	13.90	11.70
0.002	16.30	14.44	11.90

Characterisation of the Samples.—The molecular weights of the polymer samples were determined by osmotic pressure measurements in dimethylformamide and found to be 2,20,000 for sample A and 2,88,000 for B.

The equivalent weight of the polymer base B was determined by potentiometric titration in phenol-chloroform solution with $N/25$ HCl in propyleneglycol-chloroform. Glacial acetic acid could not be used as a titration medium since the salt formed in

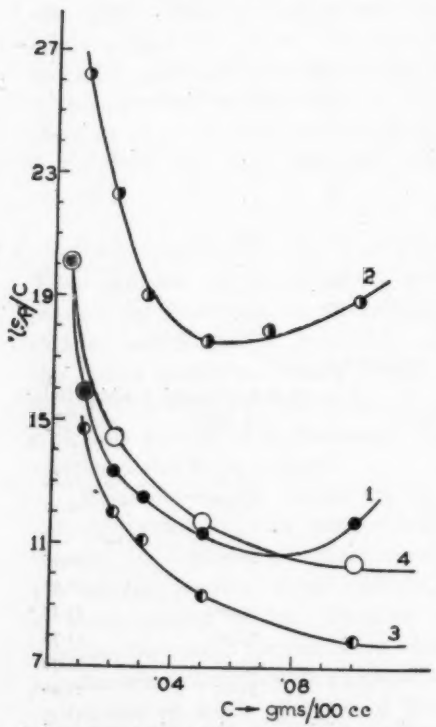
course of the titration separated out in the form of a rubbery precipitate. The equivalent weight, determined as above, was found to be about 110 as compared with the theoretical value of 105 for vinylpyridine. If we rule out the possibility of the presence of any spurious impurity in the polymer sample, the high value of the observed equivalent weight may be taken to indicate that roughly 5% of the pyridine groups in the chain have become inert with regard to basic character, presumably as a result of atmospheric oxidation. The brown colour of the sample perhaps lends some support to this conclusion. No further purification of the samples was, however, attempted.

Discussion

Viscosities in Acetic Acid and Polyelectrolytic Nature of the Polymer.—Viscosities of samples A and B were measured in glacial acetic acid at polymer concentrations in the range of 0.01-0.1 g./100 c.c. Results are presented in Table I and graphs of reduced viscosities *versus* polymer concentrations are snown in Fig. 1 (curves 1 and 2). It will be seen that the curves are not inear as in the case of neutral polymers, but show a sharp rise at the dilute end and are reminiscent of polyelectrolytes. It may be mentioned in this connection that in non-acidic solvents like chloroform, alcohol, methylethyl ketone, etc., polyvinylpyridine exhibits normal viscometric character.

Fig. 1

Viscosity of samples A and B in acetic acid.



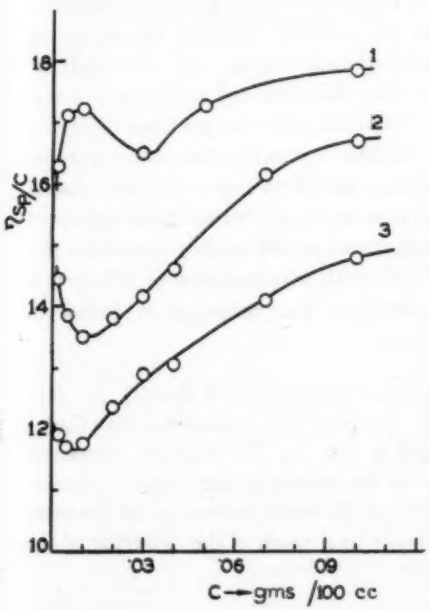
1. Sample A in acetic acid.
2. Sample B in acetc acid.
3. (1) + 0.3% Ac_2O.
4. (2) + Do.

That polyvinylpyridine does exist as an electrolyte in acetic acid solution, was confirmed by conductance measurements on sample B over the concentration range of 0.06-0.47 g. /100 c.c. The results are represented in Table II. If the equivalent conductance is plotted against the square root of the concentration, the nature of the curve obtained is found to be essentially similar to that for a weak electrolyte in water or any electrolyte in glacial acetic acid medium (Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, **56**, 1014). The curve does not provide any specific information about the nature of the ionic species in solution and, hence, is not shown here. But the results definitely indicate that the polymer base does give rise to ions in solution, though the degree of dissociation is naturally very small. In a medium of such a low

dielectric constant, the magnitude of interionic forces should, however, be very great despite a very low concentration of free ions. Thus, the repulsion between the positively charged centres on the polymer chain, though sparsely distributed thereon, will be of sufficient magnitude to cause it to exhibit the characteristic properties of a typical polyelectrolyte. Moreover, intermolecular, apart from intramolecular, electrostatic forces may be expected to play an important role in a medium of low dielectric constant. In relatively concentrated solutions of the polymer, intermolecular repulsive forces between charged centres should tend to inhibit the dilatation of the polymer coils, and these forces naturally become less significant on dilution of the polymer solution, resulting in a rise in viscosity at high dilution.

FIG. 2

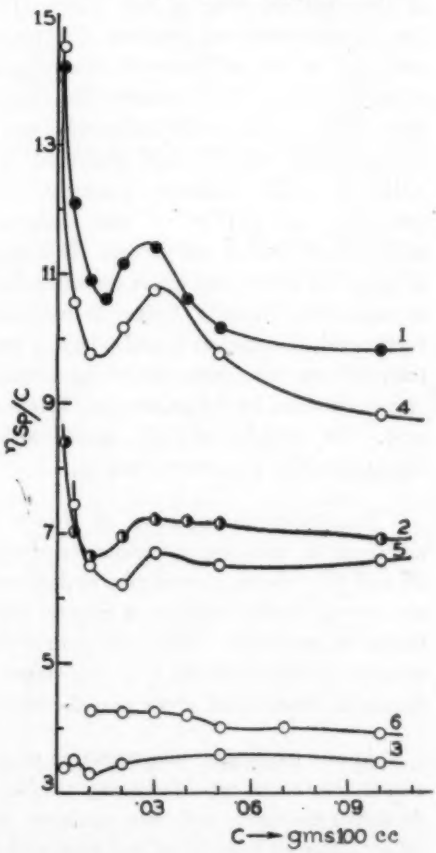
Viscosity of sample B in aq. acetic acid.



Curves 1-3 refer respectively to 5%, 10% and 20% water.

FIG. 3

Viscosity of sample B in presence of NaAc and pyridine.



Conc. of NaAc (*N*) : (1) $2.44.10 \times 10^{-4}$; (2) 24.4×10^{-4}; (3) 0.228
Conc. of pyridine (*N*): (4) 2.53×10^{-4}; (5) 25.3×10^{-4}: (6) 0.316.

It ought to be emphasised at this stage, however, that the whole idea as to the polyelectrolytic nature of the compound will be justified only if the polymer is mole-

cularly dispersed in solution. Unfortunately, it has not been possible to establish this point, since osmotic pressure method could not be applied. It should also be borne in mind that the electroviscous effect (Smoluchowski, *Kolloid Z.*, 1916, **18**, 190) might play a relatively important role in a medium of such low dielectric constant, this effect being superimposed on the folding-unfolding phenomenon as exhibited by the polyelectrolyte. From the general trend of the results, however, especially with regard to the effect of added acetates on the viscosity (reported below), it would be quite reasonable to conclude that poly-2-vinylpyridine essentially behaves as a typical polyelectrolyte in acetic acid solutions.

Viscosities in presence of Added Water.—The viscosities of sample B were measured in acetic acid containing 5, 10 and 20% water by volume respectively. The reduced viscosity is found to be progressively lowered by increasing the water content of the medium (Fig. 2 and Table III). This may arise from an increase in acetate ion concentration on addition of water, which represses the viscosity of the polyelectrolyte just as the addition of counter-ions would be expected to do in the case of any polyelectrolyte. To eliminate the effect of small amounts of water in the solvent, if any, about 0.3% acetic anhydride was added to the glacial acetic acid and viscosities of samples A and B were measured in this as the solvent. Results are shown in Table I. The reduced viscosity *versus* concentration curve for this solvent (curves 3 and 4, Fig. 1) was found to be lower than that obtained with glacial acetic acid without added anhydride. It is very likely, therefore, that the presence of traces of water in acetic acid raises the viscosity, but on further increasing the concentrations of water, the viscosity falls. It will be further observed from Fig. 1 that for glacial acetic acid, the curves 1 and 2 have a tendency to pass through minima in the region of intermediate concentrations of the polymer, and in this respect closely resemble the curves obtained by Schaefgen and Trivisonno (*loc. cit.*) with polyamides in 99.5% formic acid. On addition of 0.3% acetic anhydride, however, the minimum is found to disappear (Fig. 1, curves 3 and 4).

Viscosities in presence of Added Counter-ions.—Viscosities of sample A were measured in presence of various concentrations of pyridine and sodium acetate (Tables IV and V). Some representative data are indicated in Fig. 3. The reduced viscosities are lowered bythe addition of counter-ions and go on decreasing as the acetate concentration is increased. Thus, the counter-ions here act in the same manner as in the cases of other polyelectrolytes, *i. e.*, they lower the viscosity as a result of the lowering of the degree of dissociation of the polyelectrolyte.

At any particular concentration of pyridine or sodium acetate, the reduced viscosity slowly increases on decreasing polymer concentration, passes through a maximum, decreases thereafter and rises again on further dilution. The nature of the curves is rather different from those obtained with polyelectrolytes in general, and the appearance of a minimum in the dilute end of the curve is difficult to explain on the basis of the current theory of polyelectrolytes. The apparrent anomaly might, however, arise from traces of water present in the acetic acid used as the solvent.

TABLE IV

Effect of pyridine on viscosity.

Sample A.

Conc. (g./100c.c.)	η_{sp}/C in presence of pyridine*. (0.3165).	(0.0633).	(0.0127).	(0.00253).	(0.00025).
0.10	3.90	3.97	4.80	6.57	8.80
0.07	4.02	4.16	4.63	...	...
0.05	4.06	4.74	4.86	6.50	9.75
0.04	4.20	...	...	...	...
0.035	...	5.01	...	...	...
0.03	4.26	4.87	5.00	6.70	10.75
0.02	4.27	6.34	6.32	6.20	10.15
0.01	4.29	9.02	8.67	6.50	9.76
0.005	...	14.50	13.57	7.45	10.58
0.002	...	...	...	...	14.50

* The concentrations (g. equiv./litre) of pyridine are shown in parenthesis at the heads of the respective column

TABLE V

Effect of sodium acetate on viscosity.

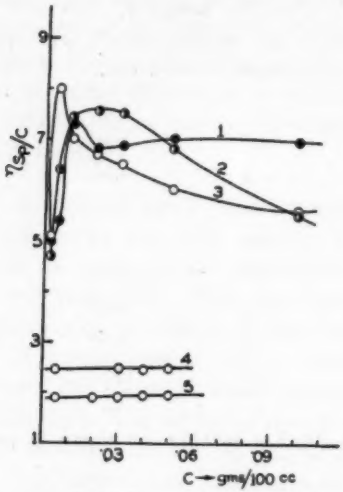
Conc. of polymer. (g./100 c.c.)	η_{sp}/C in presence of sodium acetate*. (0.228).	(0.0244).	(0.0122).	(0.00244).	(0.00024).
		Sample A.			
0.10	3.44	4.45	4.40	6.92	9.80
0.05	3.60	4.20	...	7.13	10.16
0.04	...	...	...	7.20	10.60
0.03	...	4.07	4.68	7.22	11.39
0.02	3.44	3.90	4.61	6.95	11.15
0.015	...	...	...	...	10.60
0.010	3.30	4.10	4.75	6.65	10.91
0.007	...	...	5.75	...	...
0.005	3.50	5.80	6.95	7.03	12.00
0.002	3.40	...	8.60	8.40	14.40

* The concentrations (g. equiv./litre) of sodium acetate are given in parenthesis at the heads of the respective column.

To eliminate water as far as practicable, a highly purified sample of acetic acid was prepared by repeated freezing. The viscosities of sample B were measured in this freshly prepared solvent in presence of sodium and barium acetates. The results are shown in Fig. 4.

FIG. 4

Viscosity of sample B in presence of NaAc *and* BaAc.



(1) $2.44 \times 10^{-4}N$-NaAc. (2) $1.56 \times 10^{-4}N$-BaAc.

(3) $1.56 \times 10^{-4}N$-BaAc+0.1% water.

(4) 0.227*N*-NaAc. (5) 0.172*N*-BaAc.

The graphs (Fig. 4) exhibit the normal features as usually obtained with polyelectrolytes in presence of added counter-ions. At concentrations 2.44×10^{-4} g. eq./litre of sodium acetate and 1.56×10^{-4} g. eq./litre of barium acetate the graphs (curves 1 and 2) show the expected maxima and at higher concentra-tions of acetate (0.227 g. eq./litre of sodium acetate and 0.172 g. eq./litre of barium acetate) the graphs become linear (curves 4 and 5), indicating that the polyelectrolyte character of the polymer has been completely suppressed. To test the effect of traces of water, viscosities were measured in presence of 1.56×10^{-4} g. eq./litre of barium acetate in acetic acid containing 0.1% added water. The reduced viscosities (curve 3) were found to be appreciably affected by the addition of even this small amount of water, as would be seen by comparing curves 2 and 3 in Fig. 4. The apparent anomalies presented by some of the data reported above presumably arise from the presence of traces of water in the acetic acid used as the solvent, which introduce uncertain factors in the observed results. This makes a thorough interpretation of the viscosity data rather difficult, unless experiments are carried out under absolutely anhydrous conditions.

The authors are indebted to Prof. Santi R. Palit for his interest in the work and helpful suggestions.

INDIAN ASSOCIATION FOR THE
CULTIVATION OF SCIENCE,
CALCUTTA-32.

Received April 10, 1956.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

SHORT NOTES

THE SOLUBILITY OF LEAD MONOXIDE IN PERCHLORIC ACID AND THE FORMATION OF BASIC LEAD PERCHLORATE IN SOLUTION.

By R. K. Pattanaik and S. Pani

From the study of lead iodate in perchloric acid and sodium perchlorate solution appreciable hydrolysis of Pb^{2+} to $PbOH^+$ has been observed. The first-stage hydrolysis (reaction 1) is almost complete in neutral solution (Misra and Pani, this *Journal*, 1957, **34**, 387).

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Out of the two well-known soluble salts of lead, the nitrate is not hydrolysed to any appreciable extent, but the acetate in dilute aqueous solution is hydrolysed to basic lead acetate. The hydrolysis in nitrate solution is probably prevented by the formation of nitrato lead complex. Acetate ion also forms complex with lead and still hydrolysis takes place, and the behaviour may be ascribed to two reasons: (*i*) acetic acid being a weaker acid compared to nitric acid, the salt of the former is more hydrolysed and (*ii*) the nitrato lead complex is probably a more stable complex than the acetato complex in aqueous solution. If the former is valid, lead perchlorate being a salt of a very strong acid is expected to be very little hydrolysed.

To verify this assumption, the solubility of lead monoxide in perchloric acid was studied. In the preparation of pure lead perchlorate Willard and Kessner have observed that a large excess of lead monoxide, over the amount required to give lead perchlorate, dissolves in perchloric acid solution (*J. Amer. Chem. Soc.*, 1930, **52**, 2402). It would be interesting to study this quantitatively. The solubility of lead monoxide in perchloric acid solution of different concentrations but of the same ionic strength was studied at 35°. G. R. quality lead monoxide was used in the investigation. The purity of the sample was further confirmed by estimating the lead content of the sample as lead sulphate. Perchloric acid and sodium perchlorate used were Analar quality reagents.

Perchloric acid of different but known concentrations containing calculated amount of sodium perchlorate to give the ionic strength 0.3 was used as solvent. Excess of lead monoxide was added and the mixture was heated to nearly 40-45° on a water-bath and placed in a thermostat at 35° for over a month. The lead contents of the filtrates were determined as sulphate (gravimetrically) and also as chromate (volumetrically). The results obtained by the two methods are in good agreement. The concentration of perchloric acid, which dissolved the lead oxide, was estimated as follows. A known volume of the filtrate was saturated with hydrogen sulphide and after complete precipitation of lead as sulphide it was filtered and hydrogen sulphide was boiled off from the filtrate. The acid present was estimated by titrating

against standard alkali. The results thus obtained are shown below. The square bracket indicates molar concentration per litre of solution. p_H of the solution was also measured.

TABLE I

Solvent.		Solution.		
$[HClO_4]$.	$[NaClO_4]$.	[Pb].	$[HClO_4]_2$	p_H
0.30	0.00	0.281	0.290	6 08
0.25	0.05	0.242	0.243	6.08
0.20	0.10	0.194	0.184	...
0.10	0.20	0.094	0.093	6.47

There is a slight variation in the strength of the acid originally taken $[HClO_4]_1$ and the strength of the acid $[HClO_4]_2$ obtained after precipitation of lead as sulphide. This is probably due to a slight change in volume caused by mixing of solutions of sodium perchlorate and perchloric acid. The results, however, definitely indicate the presence of lead and perchlorate in the solution in the ratio 1 : 1. The solution is very nearly neutral ; the solid phase though white in colour is free from perchlorate, as indicated by drying a sample at 120° and analysing for its lead content. The dry solid is lead monoxide. The white solid in equilibrium with the solution is most probably hydrated lead oxide or lead hydroxide. The reaction may be represented by equation (2), assuming perchlorate ion to have no capacity to form complex.

$$Pb(OH)_2 + H^+ = PbOH^+ + H_2O \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

In neutral solution and in absence of complex-forming ligands, lead exists as $PbOH^+$ in aqueous solution. Lead monoxide behaves as a strong mono-acidic base.

The authors are grateful to B.S.I.R. for a grant to enable them to purchase chemicals. One of them (Pattanaik) is thankful to the Utkal University for the award of a research scholarship. The authors are also thankful to the authorities of the Ravenshaw College for providing them with the facilities to work.

DEPARTMENT OF CHEMISTRY,
RAVENSHAW COLLEGE,
CUTTACK-3.

Received June 3, 1957.

PARACHOR OF ORTHOPHOSPHORIC ACID

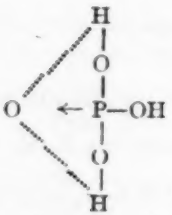
By V. G. Vaidya and B. K. Maheshwari

Vaidya and co-workers (*J. VK. Univ.* 1957, **1**, 73 ; *Agra Univ. J. Res.*, 1956, 5-II) have studied parachor of nitric and sulphuric acids and have established intramolecular hydrogen bonds in them. A similar study of orthophosphoric acid of strengths 15.87 *M* to 2.55 *M* has been undertaken. The results are shown below.

Table I

Conc.	Temp.	x.	M_m.	d.		P_m.	P_x.
15.87 *M*	21.6°	0.5977	65.811	1.747	82.87	113.70	154.7
14.71	22.2°	0.5069	58 546	1.698	81.70	103.60	153.2
13.61	21.0°	0.4358	52.870	1.651	79.52	95.61	151.3
13.03	23.0°	0.4017	50.130	1.628	80.19	92.19	151.1
12.00	21.7°	0.3490	45.920	1.580	81.02	87.20	151.7
11.03	18.9°	0.3026	42.200	1.538	80.19	82.12	150.3
10.27	23.6°	0.2714	39.710	1.502	80.69	79.25	150.8
9.40	23.0°	0.2388	37.110	1.462	79.23	75.75	149.6
8.55	22.0°	0.2085	34.690	1.422	78.96	72.68	148.9
7.50	21.5°	0 1748	31.990	1.373	75.91	68.79	145.2
6.79	20.6°	0.1537	30.300	1 340	76.15	66.80	145.0
6.16	21.7°	0.1361	28.890	1.309	75.78	65.13	144.7
2.55	25.8°	0.0435	21.482	1.114	74.20	56.59	144.4

The value of parachor for strongest solution of the acid is found to be 154.7. Arbuzov and Vinogradova (*Izvest Akad. Nauk, SSSR, Otdel Khim. Nauk*, 1951, 733) have found the parachor of esters of phosphoric acid and Vogel (*J. Chem. Soc.*, 1948, 1804) that of orthophosphate group. The parachor of orthophosphoric acid calculated indirectly from their values is 155.16 which closely agrees with the value obtained by us. The parachor calculated for the acid is 167.6, showing a drop of 13 units in the observed value. Several communications from this laboratory (this *Journal*, 1944, **21**, 53, 62 ; 1952, **29**, 679) show that there is a parachor drop due to ionisation and hydrogen bonding. Nims (*J. Amer. Chem. Soc.*, 1933 **55**, 1946 ; 1934, **56**, 1110) has found the values for K_1 and K_2 of the acid to be 8.95×10^{-3} and 6.056×10^{-8} respectively. Smith ("Analytical Processes—A Physico-chemical Interpretation", 1949, p. 445) records the value of K_3 to be 4.8×10^{-13}. It is therefore quite obvious that there is very little ionisation in the strongest acid. Therefore, the parachor drop can be ascribed to hydrogen bonding only. The acid can therefore be represented as



Venkateswaran (*Proc. Ind. Acad. Sci.*, 1938, **7A**, 13) from the study of Raman spectra of disodium hydrogen phosphate has found the presence of a hydrogen bond in the compound. Hendricks (*Amer. J. Sci.*, 1927, **14**, 269) and West (*Z. Krist.*, 1930, **74**, 306) have established the presence of hydrogen bonds in potassium dihydrogen phosphate crystals from crystallographic studies. It is thus reasonable to assume that two intramolecular hydrogen bonds exist in the orthophosphoric acid molecule. Our results confirm this.

The value of parachor drops from 154.7 at 15.87 *M* to 144.4 at 2.55 *M*. This drop is due to gradual and regular ionisation.

The authors wish to thank Dr. S. N. Kaveeshwar for his valuable suggestions and keen interest in the work.

CHEMICAL LABORATORY,
HOLKAR COLLEGE, INDORE.

Received May 3, 1957.

[Jour. Indian Chem. Soc., Vol. 34, No. 9, 1957]

ON THE COMPOSITION OF SILVER CITRATE

By Krishna C. Mathur and Arun K. Dey

In previous communications (Dey, *Compt. rend. Acad. Sci., U.S.S.R.*, 1947, **53**, 1047 ; *J. Coll. Sci.*, 1948, **3**, 473) the formation of a soluble complex between silver and citrate ions has been described. When a soluble citrate is added to a silver nitrate solution, a white curdy precipitate is obtained, which dissolves in excess of citrate, forming the argentocitrate complex (Mukherji and Dey, *Anal. Chim. Acta*, 1955, **12**, 501 ; *Z. anal. Chem.*, 1955, **145**, 94). The composition of the precipitated silver citrate seems to have remained uninvestigated and it is considered worthwhile to investigate its composition. A similar precipitate is also formed by adding sodium, potassium or ammonium hydroxide solution to the colorless solution obtained by dissolving silver citrate in an excess of citric acid solution. In this note we have found the composition of the white curdy precipitate to be Ag_3Cit in every case.

Procedure.—Standard solutions of silver nitrate, sodium citrate, citric acid and sodium, ammonium and potassium hydroxides were prepared using BDH-Analar reagents and dissolving in double-distilled water. All the solutions were standardised by the usual methods.

In the first set of experiments 25 c.c. of 0.125 *M* silver nitrate was taken and 1 *M* solution of sodium dihydrogen citrate was added dropwise till precipitation was complete. The precipitate was kept overnight, filtered in a sintered glass crucible and was thoroughly washed with water. The precipitate was dried in an air-oven at 100-110°, and then analysed for its silver content which was found to be 62.39% (Ag calc. for Ag_3Cit : 63.13%).

In a second set of experiments equal volumes of 0.125 *M* silver nitrate and 1 *M* citric acid were mixed and to the mixture varying amounts of 2 *M* sodium, potassium or ammonium hydroxide were added. The precipitates obtained were washed and analysed after drying. In every case, the composition was found to be Ag_3Cit.

It is thus concluded that the precipitate in all cases is Ag_3Cit, *i.e.*, silver replaces carboxylic hydrogen in citric acid to produce the insoluble citrate, and that the hydroxylic hydrogens are not involved in the formation of precipitated silver citrate. It is also evident that the soluble argentocitrate is unstable in presence of alkali and is decomposed to silver citrate on the addition of hydroxyl ions. Further work on complex citrates is in progress.

The authors are thankful to the Scientific Research Committee, U. P. Govt., for supporting the work and for the award of a research assistantship to one of them (K.C.M.).

Chemical Laboratories,
University of Allahabad,
Allahabad-3

Received July 15, 1957.

A Monumental Work *Published March 1956*

A book that should find place on the shelves of every Library

HISTORY OF CHEMISTRY IN ANCIENT & MEDIEVAL INDIA

Incorporating

HISTORY OF HINDU CHEMISTRY

by Acharya Prafulla Chandra Ray

Edited by PROF. P. RÂY

Royal 8*vo*. Rexin bound, 494 pages with 39 illustrations.

Price *ex*-postage: Prime Edition:—Rs. 24/- (Inland), Ordinary Edition—Rs. 20/- (Inland)
£ 2/- or $ 6.00 (Foreign)

For Fellows „ „ Rs. 20/- „ „ Rs. 16/-

An invaluable book for students of science and history and to all persons interested in the scientific heritage of India.

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY

92, Upper Circular Road, Calcutta-9, INDIA.

Some Opinions:

Nature, January 5, 1957.

"Since there is much new material in the book, all those who are fortunate enough to have the earlier edition will wish to have the new one. ... ...

"All those interested in the History of Chemistry owe a debt of gratitude to Prof. P. Rây and the Indian Chemical Society for its publication".

J. R. Partington.

Journal of Chemical Education, February, 1957:

"..... Professor Ray, in his carefully constructed revision of Prafulla Chandra Ray's standard 'History of Hindu Chemistry' has given us a highly informative and interesting description of Indian Chemistry. In chronological order, the contributions of Indians to chemistry have been recorded from the Harappa period of the fourth millennium B.C. to the end of Mogul culture..... Many of the ideas described make delightful reading for the average chemist with a historical bent..... chemists and historians of chemistry will find in this book a valuable assessment of ancient Indian chemistry and culture".

SETA

Petroleum Testing Equipment

*Aniline Point *Breaking Point of Bitumen *Smoke Point *Burning Test *Carbon Residue *Cloud and Pour Point *Anti-rust Characteristics *Free Sulphur *Drop Point *Distillation *Electric Strength * Existent Gūm *Evaporation Loss *Flash Point *Foaming Characteristics *Oxidation *Oxidation Stability *Penetration *Specific Gravity *High Temperature Performance *Leakage Tendency *Wear *Rolling Stability *Water Wash-out *Sulphur Content *Oil Content *Softening Point *Setting Point *Sediment *Vapour Pressure *Viscosity

etc. etc.

GORDHANDAS DESAI PRIVATE LTD.

PHEROZESHAH MEHTA ROAD, BOMBAY 1.

P-7, Mission Row Extension, CALCUTTA 1. **4/2B, Asaf Ali Road, NEW DELHI.** **22, Linghi Chetty Street, MADRAS 1.**

S.P./GD/65

SPECIALLY MADE

Apparatuses

For

* BOILING POINT TEST

* FREEZING POINT TEST.

* ARSENIC TEST.

B. P. (1953) Standard.

Please Enquire to

SCIENTIFIC GLASS APPARATUS MFG. CO.

11/2 Harinath Dey Road, Calcutta-9

Phone : Rasf. 4411. Gram : Sigamko,

BOROSIL

LABORATORY GLASSWARE

such as

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE TO DESIGN

and

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

INDUSTRIAL & ENGINEERING APPARATUS CO. PRIVATE LTD.

CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.

INDEX SIGCOL

DO YOU KNOW

Sigcol **Index** combines **three** in one ? Behind every **Index** beaker and flask you can see long experience backed by scientific research. **Index** is a symbol of guarantee for laboratory work. It is

* Resistant to Chemical reagents

Resistant to mechanical shocks

* Resistant to heat (coefficient of expansion is only 3.4 10^{-6}).

Sole Distributors :

GHARPURE & CO

P-36, Royal Exchange Place Extn.

Calcutta 1

For Laboratory *Reagent Quality* Acids

To Precise Specifications

Maximum Limits of Impurities:	Acid Sulphuric H_2SO_4:98% w/w Sp. gr. 1.840 at 15°.	Acid Nitric HNO_3:69.8% w/w Sp.gr. 1.420 at 15°.	Acid Hydrochloric HCl:35.39% w/w Sp. gr. 1.18 at 15°
Non-Volatile Matter :	0.0025 %	0.001 %	0.0015 %
Chloride (Cl) :	0.0003 %	0.0001 %	—
Free Chlorine (Cl) :	—	—	0.0002 %
Nitrate (NO_3) :	0.00002 %	—	—
Iodate (IO_3) :	—	0.0005 %	—
Sulphate (SO_4) :	—	0.0003 %	0.0003 %
Heavy Metals (Pb) :	0.0002 %	0.0002 %	0.0002 %
Iron (Fe) :	0.0001 %	0.0001 %	0.0001 %
Arsenic (As_2O_3) :	0.00001 %	0.05 part per million	0.04 part per million
Ammonia (NH_3) :	0.0005 %	—	—
Oxygen Absorbed (O) :	1.0001 %	—	—

We invite orders and enquiries.
Write us about your requirements for other reagent quality chemicals.

Bengal Chemical & Pharmaceutical Works, Ld.

CALCUTTA :: BOMBAY :: KANPUR

Office : 6, Ganesh Chunder Avenue, Calcutta-13

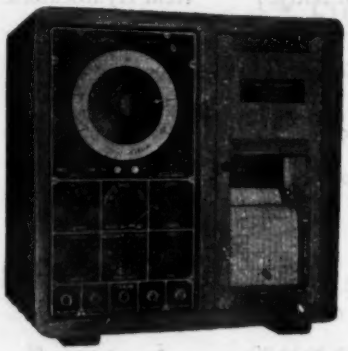
FOR RAPID & ACCURATE CHEMICAL ANALYSIS

USE

TINSLEY

POLAROGRAPH (with derivative circuit)

Here are some advantages :



* MICRO ANALYSIS
* HIGH SENSITIVITY
* QUALITATIVE AND QUANTITATIVE ESTIMATION
* SIMULTANEOUS ESTIMATION OF SEVERAL CONSTITUENTS ON ONE POLAROGRAM
* ADAPTABILITY : ANALYSIS OF METALS, ORGANIC & INORGANIC SUBSTANCES ON THE SAME SAMPLE
* REPEATED ANALYSIS
* SIMPLIFIED OPERATION FOR USE BY SEMI-SKILLED STAFF
* ROUTINE ANALYSIS WITH SPEED AND ACCURACY.

For further particulars, please contact Sole Agents in India

PIONEER EQUIPMENT CO. PRIVATE LTD.

(Formerly Pioneer Industries)

1, Mango Lane, CALCUTTA-1.

139, Medows Street, (Ground Floor) P. O. Box. 1909, BOMBAY-1.

193, Mount Road MADRAS-2.

*** FOR YOUR REQUIREMENTS OF ALL KINDS OF EQUIPMENTS FOR RESEARCH ***

RAJ-DER-KAR & CO.,

231, HORNBY ROAD, FORT, BOMBAY-1

Telephone : 26-2304
Telegram : 'TECHLA

A few of our Agencies :

* LUDWIG SEIBOLD, Austria, For p_H Testers, Titrators, and Recorders etc.

* EASTMAN KODAK, U. S. A., For All Sorts of Complex Organic Chemicals.

* W.A. TAYLOR & CO., U. S. A. For p_H Comparators, Indicators, Water Analysers etc.,

* TRACERLAB Inc., U. S. A., For Radiochemicals & Equipment for Nuclear Research.

Phone—34-8176. Telegrams—Nadiachemi.

NADIA CHEMICAL WORKS PRIVATE LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA

Manufacturers of :—

1. *CHEMICALS*—**Benzene, Toluene, &c., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals.**
2. **STILLS for distilling Essential Oils, Alcohols, Water, etc.**

   RECTIFIERS, CONDENSERS, &c.
3. **OVENS, Baths &c for Gas, Oil or Electric heatings.**
4. **Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, &c.) of both Glass and Metal.**
5. **MICRO-ANALYSIS APPARATUS.**

Please ask for Estimates.

AVAILABLE FROM READY STOCK

** AEROGEN GAS PLANT
** GERMAN IKA LABORATORY STIRRERS
** CAMBRIDGE BENCH PATTERN pH METER
** CAMBRIDGE ELECTRODES (ALL TYPES)
** QUICKFIT & QUARTZ GROUND GLASS JOINT ASSEMBLIES
** EVERYTHING IN PYREX AND GERMAN GLASSWARE

Direct your enquiries to:

LABORATORY FURNISHERS

DHUN MANSION, VINCENT ROAD, DADAR, BOMBAY 14.

Grams: 'LABFURNISH' BOMBAY-DADAR. Phone: 62761.

Branch: AHMEDABAD.

VERY RELIABLE INDIGENOUS SUBSTITUTES OF GUARANTEED ANALYTICAL REAGENTS MAY BE FOUND IN

"BASYNTH"
Brand
ANALYTICAL REAGENT

Acid Hydrochloric
Acid Hydrochloric Fuming
Acid Sulphuric
Acid Nitric
Acid Nitric Fuming
Acid Acetic Glacial
Ammonium Hydroxide
Benzene
Toluene
Xylene
Petroleum Ether
Amyl Alcohol
Butyl Alcohol Etc., Etc.

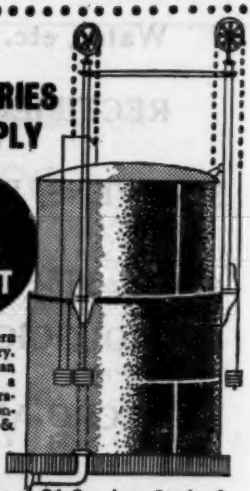
BASIC & SYNTHETIC CHEMICALS PRIVATE LTD
P. O. Jadavpur College, Calcutta-32

GS Gas PLANTS
FOR
HEATING
IN
LABORATORY
INDUSTRY
KITCHEN

GANSONS
PRIVATE LIMITED.
P.O.B. 5576, BOMBAY-14.
——**Also makers of**——
Superior Laboratory Fittings
Atomic Equipments.

For LABORATORIES GAS SUPPLY

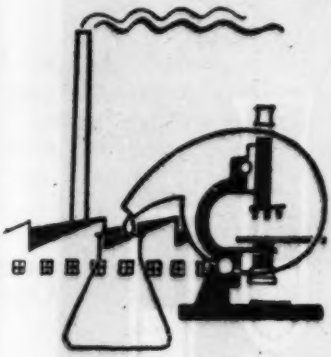
OIL GAS PLANT



—a must for a modern Laboratory and Industry. We have at our back an experience of many a years in serving Laboratories & Industrial concerns all over India & abroad.

Our Specialities—Fitting of Oil Gas plants, Supply of Science Laboratory Equipments, Furniture & Wood work of all descriptions.

MANSFIELD OIL GAS CO. LD
16, RADHANATH CHOWDHURY ROAD, CALCUTTA-15
Branch—301, LINGHI CHETTY ST., MADRAS 1.



SERVING for LAST 40 YEARS

Laboratory Chemicals & Reagents

of a wide range are manufactured by us under expert supervision to ensure guaranteed standard & reliability.

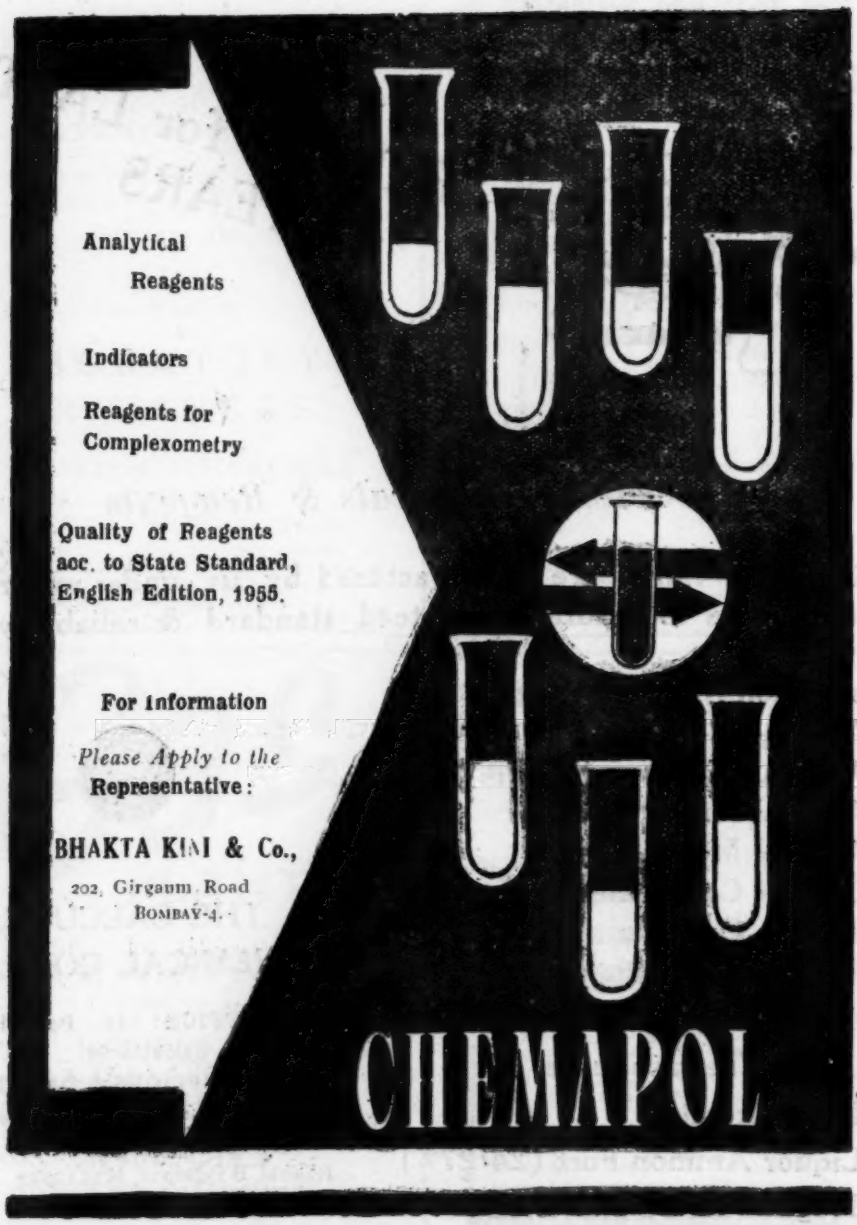
A selection from our range :

Acetone
Acid Acetic glacial 99-100%
Alcohol Amyl
Alcohol Methyl
Barium Carbonate
Barium Chloride
Benedicts' Solution
Benzene
Carbon Tetrachloride
Lead Acetate
Liquor Ammon Fort (24/27%)
Magnesium Sulphate XL

THE CALCUTTA CHEMICAL CO., LTD.

HEAD OFFICE: 35, Panditia Road, Calcutta 29.

BRANCH OFFICES & DEPOTS AT: Delhi, Madras, Bombay, Bangalore, Vizag., Nagpur, Jamshedpur, Patna, Ranchi, Bhagalpur, Madhupur, Asansol, Siliguri.



PRAHA, CZECHOSLOVAKIA

PRESIDENT :

P. K. Bose, D.Sc., F.N.I.

VICE-PRESIDENTS :

(who have filled the office of President)

N. R. Dhar, D.Sc., Dr.rs.Sc., F.R.I.C., F.N.I.
B. B. Dey, D.Sc., F.R.I.C., F.N.I.
Sir J. C. Ghosh, Kt., D.Sc., F.N.I.
B. C Guha, D.Sc., Ph.D., F.N.I.
P. C. Guha, D.Sc., F.N.I.
J. N. Mukherjee, C.B.E., D.Sc., F.A.S.B., F.N.I.
Mata Prasad, D.Sc., F.R.I.C., F.N.I.
J. N. Ray, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. Rây, M.A., F.N.I.
B. K. Singh, Sc.D., F.R.I.C., F.N.I.

VICE-PRESIDENTS :

U. P. Basu, D.Sc., F.N.I.
B. Sanjiva Rao, D.Sc., Ph.D., F.N.I.
K. Venkataraman, D.Sc., Ph.D., F.R.I.C., F.N.I.
R. D. Desai, D.Sc., F.R.I.C., F.N.I.
President of Ahmedbad Branch (*ex-officio*)

HONY. SECRETARY :

M. M. Chakrabarty, M.Sc., Ph.D.

HONY. TREASURER :

B. N. Ghosh, D.Sc., F.N.I.

MEMBERS OF THE COUNCIL :

N. Adhikari, M.Sc.
D. K. Banerjee, D Sc.
D. Chakravarti, D Sc., F N.I.
Mrs. Ashima Chatterjee, D.Sc.
B. Chatterjee, D.Sc.
A. C. Chatterji, D.Sc., Dr. Ing., F.N.I.
H. N. Das Gupta, D.Sc.
S. S. Joshi, D.Sc., F.R.I.C., F.N.I.
T. N. Ghosh, D.Sc., F.N.I.
J. Gupta, D.Sc.
A. N. Kappanna, D.Sc , F.N.I.
S. M. Mehta, M.Sc, F.A.Sc., A.R.I.C.
R. P. Mitra, D.Sc., F.N.I.
S. M. Mukherji, D.Sc., Ph.D.
S. N. Mukherjee, D.Sc.
P. V. Nair, M.Sc., D.Phil.
A. B. Sen, M.Sc., Ph.D.
V. Subrahmanyan, D.Sc., F.R.I.C , F.N.I.
L. M. Yeddanapalli, M.A., Ph.D., D.Sc., F.R.I.C.
S. H. Zaheer, M.A., Ph.D.

HONY. EDITORS :

S. R. Palit, D.Sc., F.R.I.C., F.N.I.
R. C. Shah, D.Sc., F.N.I.

BOARD OF ASSOCIATE EDITORS :

D. K. Banerjee, D.Sc.
P. K. Bose, D.Sc., F.N.I.
B. Chatterjee, D.Sc.
J. K. Chowdhury, M.Sc., Ph.D., F.N.I.
P. C. Dutta, D.Sc.
B. N. Ghosh, D.Sc., F.N.I.
J. C. Ghosh, D.Sc., F.N.I.
A. N. Kappanna, D.Sc., F.N.I.
S. K. Mukherjee, D.Sc.
B. C. Guha, D.Sc., Ph.D., F.N.I.
P. Ray, M.A., F.N.I.
T. R. Seshadri, M.A., Ph.D., F.N.I.
P. B. Sarkar, Dr.rs. Sc., F.N.I.
K. Venkataraman, D.Sc., Ph.D., F.N.I.

HONY. AUDITORS :

P. C. Nandi, M.A., B.Sc., A.C.A.R.A.
A. B. Gupta, B.Sc., L.L.B., A.C.A.R.A.

Asst. Secretary:
B. C. Roy, M.Sc.

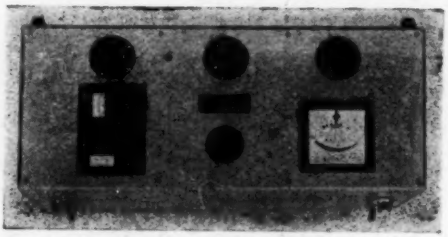
Asst. Editor:
G. Banerjee, M.Sc.

Regtd. No. C1878

EX: MESSRS. WISSENSCHAFTSLICHE TECHNISCHE WERKSTATTEN, GERMANY.

DEKAMETER TYPE DKO 3

For the Determination of Dielectric Constant and Moisture Content of substances.



The dielectric constant is very helpful in determining the purity, structure and composition of substances and can be measured from 1.8 to 100 or above with a sensitivity of 5×10^{-5} (limit of error 0.5 – 0.005%) with the Dekameter.

The instrument is specially adapted for rapid moisture determination in all substances, e. g., cereals, meal, tobacco, ceramics. Range 0 – 100%. The accuracy is high (limit of error 0.001 to 1% for liquids and 0.01 to 0.5% for solids).

The instrument is invaluable in the study and quality control of chemical processes like distillation, polymerisation, ageing, esterification and saponification.

A variety of measuring cells for liquids, solids, pastes, powders, foils are available.

Other Instruments:

Dipolemeters, Dekameters DKO 4, DKO 5, DKO 8, Moisture Meters, Conductivity Meters, p_H Meters, etc.

SOLE AGENTS:

TOSHNIWAL BROTHERS PRIVATE LTD.

198, Jamshedji Tata Road, Bombay-1

Branches:

14-B/4 N.E.A. Uttari Marg, NEW DELHI-5.

9, Blacker's Road, MADRAS-2.

31, Ballygunge Place, CALCUTTA-19

Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press., 48, Hazra Road., Ballygunge, Calcutta and Published by G. Banerjee, Esq., M.Sc., Asst. Editor., Indian Chemical Society.